Review

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Prenylated and Geranylated Derivatives of Non-Oxidized Monomeric Acylphloroglucinols of Natural Origin: Occurrence, Biological Properties and Spectroscopic Data

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Phloroglucinols comprise polyphenolic compounds abundantly present in biological systems, which are synthesized and accumulated by plants, microorganisms, and marine organisms of different families. Interesting biological activities are associated with these compounds endowed with unique structural characteristics. Because of this, they have become attractive for studies in several areas, such as chemistry and pharmacology. Despite the existence of reputable reviews on phloroglucinol and its derivative compounds, updates on the subject are constant and there are still unexplored specificities of these polyphenols in the literature. Therefore, the present review compiled data on monomeric derivatives of acylphloroglucinols isolated from natural sources. These compounds were grouped into classes considering the oxidation of the central 1,3,5-trihydroxybenzene (THB) ring. Nuclear magnetic resonance (NMR) spectroscopic data and biological activities reported in the literature were associated with the cataloged metabolites considering publications from 1965 to 2022.

Keywords: polyphenols, acylphloroglucinol, nuclear magnetic resonance, spectroscopy

1. Introduction

Phloroglucinols are polyphenolic compounds with wide occurrence in different natural sources, such as plants, microorganisms, and marine organisms. Its chemical structure is characterized by the tautomeric form 1,3,5-trihydroxybenzene (THB). However, when produced biologically, it can be converted into 1,3,5-cyclohexanetrione.[1] THB core biosynthesis occurs via the acetate-malonate pathway, starting by the conversion of acetate into acetyl coenzyme A (acetyl-CoA) catalyzed by acetyl-CoA carboxylase subunit, forming malonyl coenzyme A (malonyl-CoA) units, which are then converted into phloroglucinols via enzymatic reduction mediated by polyketide synthase.[1-4]

Phloroglucinol-derived molecules commonly have alkyl or acyl groups at aromatic carbon of the THB unit, allowing further cyclization and oxidation reactions. Because of this, polycyclic and caged structures can be formed.[1,3] The structural variability of these derivatives provides a promising source of bioactive compounds, which can serve as a basis for the development of medicinal and supplementary healthcare products.[5,6] These compounds have been associated with biological activities, such as: antibacterial, anthelmintic, antimicrobial, antioxidant, anti-angiogenic, antibiotic, and anti-human immunodeficiency virus (HIV).[1,5-15]

The information on phloroglucinols has been reported through experimental studies and compiled in literature reviews.[5,6,16-25] These reports consider their natural sources, such as Gutiferae, Euphorbiaceae, Aspidiaceae, Compositae, Rutaceae, Rosaceae, Clusiaceae, Lauraceae, Crassulaceae, Cannabinaceae, and Fagaceae families.[21] However, they are especially associated with the Hypericum and Myrtaceae families.[6,21] In addition, the occurrence of these compounds in marine organisms and microorganisms is also known.[21]

Despite the existence of respectable reviews focusing on phloroglucinol derivatives, updates on this subject are constant and there are still unexplored specificities in the literature. Therefore, the present review has compiled data about monomeric acylphloroglucinol derivatives, prenylated and geranylated, isolated from natural sources. These compounds were grouped into classes considering the substitution pattern of the THB central ring. Nuclear magnetic resonance (NMR) spectroscopic data and the biological activities reported in the literature were

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associated with the cataloged metabolites considering publications from 1965 to 2022.

2. Bibliographic Sources

This review was systematically developed by compiling data from primary studies considering the period from 1965 to 2022 and considering an inclusive criterion, in which the focus is the monomeric derivatives of acylphloroglucinol. Because of this, molecules from different biosynthetic routes, such as benzophenones, were disregarded.

The selected natural metabolites were described according to the extraction, isolation, and elucidation methods. Consequently, synthetic products and phloroglucinols without the information of interest were disregarded. Molecules were grouped and described according to their structural similarities, observing chemical, biological, taxonomic, geographic, and spectroscopic data. One-dimensional NMR signals and other information were compiled without any spectroscopic correction to the primary study material; allowing to standardize and preserve original interpretations and content since the authors were not contacted.

The platforms used in the research were: Google Scholar, ACS Publications, ResearchGate, Periodicals CAPES, Science Direct, and ScienceFinder. In addition, the keywords "phloroglucinol", "acylphloroglucinol", "acetophenone", "geranyl acylphloroglucinol", and "prenyl acylphloroglucinol" were considered in the searches.

3. Biosynthetic Aspects

Plants use secondary metabolism to their own defense against biotic and abiotic factors. Further, these products are responsible for several medicinal properties of interest.[26] The origin of acylphloroglucinols shows that the carbonyl unit is bioenergetically favored. Phloroglucinols come from a biosynthetic route where the THB nucleus is biosynthesized by the acetate-malonate pathway, starting with the conversion of acetate into acetyl-CoA.[21,27,28]

Metabolites from different classes may have type III polyketide synthases (PKSs) as biosynthetic precursors. These enzymes, initially identified in plants, are small homodimeric proteins formed by monomers containing independent active sites, and having a catalytic triad composed by cysteine, histidine, and asparagine residues; typically, these enzymes can incorporate a specific substrate to generate a poly-β-keto intermediate, which undergoes cyclization. Subsequently, various products can be obtained through a variety of condensation reactions such as the Claisen condensation.[29,30]

Furthermore, to construct a generic biosynthetic model, they relied on hyperforin through theoretical and thermodynamic insights, a polyprenylated phloroglucinol that can exist in five tautomeric forms.[31-33] Subsequently, new studies[34,35] suggested a direct correlation between the biosynthesis of phloroglucinol derivatives in plant species (such as those from the genera *Hypericum*, *Acronychia*, *Myrtaceae*) with enzymes of the type III polyketide synthase family, as also proposed to other classes of metabolites from the same bioenergetic precursors.[34,35]

Type III PKSs catalyze a sequential decarboxylative condensation of three malonyl-CoA molecules mediated by acetyl CoA to provide a linear tetracarbonyl polyketide intermediate, which then undergoes an intramolecular Claisen type condensation with loss of both native coenzyme A and enzyme. In fact, this process is similar to the aldol reaction that occurs in the cyclization of simple phenols to obtain orselinic acid as a product. Then, formation of the acylphloroglucinol proceeds via direct enolization, as shown in Figure 1. Other reactions may occur later, from the acylphoroglucinol generated, for example: intramolecular cyclization, alkylation, acylation, alkoxylation, prenylation, and geranylation.[36-39]

It is also kwon that prenyltransferase (PT) catalyzes the addition of dimethylallyl pyrophosphate (DMAPP) to the THB core.[28] These enzymes were detected in experiments involving culture of *Hypericum calycinum* cells. Furthermore, the formation of six-membered heterocyclic rings in derivatives with more than one cycle has been observed in isolated compounds of the same genus.[40]

4. Chemical and Biological Aspects

The systematic analysis of studies involving the structural characterization of prenylated and geranylated non-oxidized acylphloroglucinols published between 1965 and 2022 allowed the compilation of 139 substances, which are homogeneously distributed over the years (Figure 2). These compounds having unoxidized THB unities were textually described and subdivided into two subclasses already established in the literature: monocyclic and polycyclic derivatives.[21,22]

The metabolites were summarized in three tables over this report, and Table 1 addresses the extraction methodology and biological activities.

Cytotoxicity and antimicrobial actions stand out as the most frequently activities associated with the phloroglucinol derivatives reported in literature (Figure 3).

Cytotoxic effects in phenolic derivatives behave as a cell-dependent uptake rate directly related to their lipophilicity. This activity in polyhydroxylated phenolic

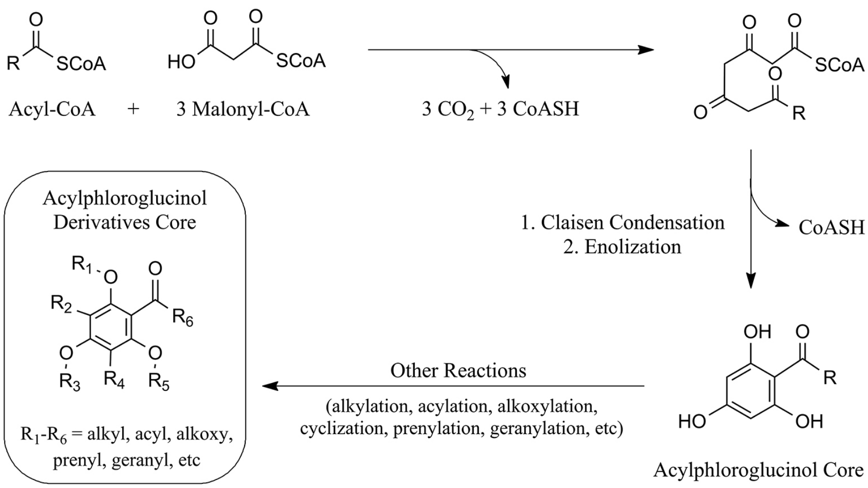


Figure 1. Proposed biosynthetic pathway for the formation of acylphloroglucinol core from malonyl CoA and further biotransformation's.

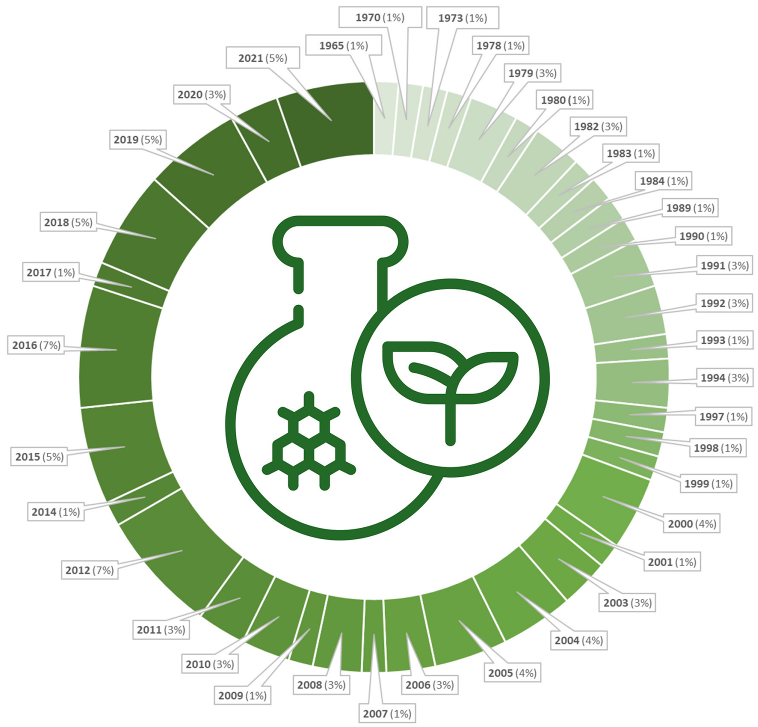


Figure 2. Percentage distribution over the years of natural acylphloroglucinols reported in the literature.

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
2,4,6-Trihydroxy propiophenone-4-*O*-3'-3'dimethylallyl ether (**1**)	*Leontonyx squarrosus* (roots, diethyl ether/petroleum ether)[41]	–
2,4,6-Trihydroxy isobutyrophenone-4-*O*-3',3'-dimethylallyl ether (**2**)	*Leontonyx squarrosus* (roots, diethyl ether/petroleum ether)[41]	–
2,4,6-Trihydroxy-2-methylbutyrophenone-4-*O*-3',3'-dimethylallyl ether (**3**)	*Leontonyx squarrosus* (roots, diethyl ether/petroleum ether)[41] *Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
1-(2-Methylbutanone)-4-*O*-prenyl-phloroglucinol (**4**)	*Helichrysum niveum* (aerial parts, CH_3OH)[42]	–
1-(2-Methylpropanone)-4-*O*-prennyl-phloroglucinol (**5**)	*Helichrysum niveum* (aerial parts, CH_3OH)[42]	–

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
4-Geranyloxy-1-(2-methylpropanoyl)-phloroglucinol (**6**)	*Helichrysum gymnoconum* (roots, diethyl ether/petroleum ether)[43] *Hypericum densiflorum*[44] *Hypericum jovis*[45]	–
2,6-Dihydroxy-4-geranyloxyacetophenone (**7**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[46] *Melicope obscura*[47]	–
4-Geranyloxy-1-(2-methylbutanoyl)-phloroglucinol (**8**)	*Helichrysum gymnoconum* (roots, diethyl ether/petroleum ether)[43] *Hypericum densiflorum*[44]	–
4-Geranyloxy-2,6,β-trihydroxyacetophenone (**9**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[46] *Melicope obscura*[47]	–
4-Farnesyloxy-2,6-dihydroxyacetophenone (**10**)	*Boronza ramose* (aerial parts, petroleum ether/ethyl acetate/CH_3OH)[48]	–
Acronylin (**11**)	*Remirea maritima*[49] *Acronychia pedunculata* (root bark, CH_2Cl_2)[50,51] *Melicope stipitate*[52] *Acronychia trifoliolata*[53] *Acronychia pubescens*[54]	–
1-(2-Methylbutanone)-3-prenylphloroglucinol (**12**)	*Helichrysum gymnoconum* (roots, diethyl ether/petroleum ether)[43] *Helichrysum niveum*[42]	–
1-(2-Methylpropanone)-3-prenylphloroglucinol (**13**)	*Helichrysum gymnoconum* (roots, diethyl ether/petroleum ether)[10,43] *Helichrysum kraussii*[55] *Helichrysum niveum*[42]	–
1-(Butanone)-3-prenyl-phloroglucinol (**14**)	*Helichrysum niveum* (aerial parts, CH_3OH)[42]	–
2-(1'-Geranyloxy)-4,6-dihydroxyacetophenone (**15**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[46]	–
2-(1'-Geranyloxy)-4,6,β-trihydroxyacetophenone (**16**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[56]	–
2,4,6-Trihydroxy-3-geranyl-acetophenone (**17**)	*Melicope ptelefolia* (leaves, CH_3OH)[57]	–
3-Geranyl-1-(2'-methylpropanoyl) phloroglucinol (**18**)	*Hypericum natalitium* (aerial parts, ether/petroleum ether)[58] *Achyrocline alata*[59] *Esenbeckia nesiotica*[60] *Hypericum styphelioides*[61] *Hypericum jovis*[45,62] *Hypericum empetrifolium*[3,63] *Hypericum* spp.[64] *Hypericum roeperianum*[65] *Garcinia dauphinensis*[66] *Hypericum annulatum*[35] *Hypericum faberi*[67] *Hypericum japonicum*[68]	–
2-Geranyloxy-1-(2-methylpropanoyl) phloroglucinol (**19**)	*Hypericum* spp. (aerial parts, acetone/CH_3OH)[64]	antimicrobial (Gram-positive bacteria)[64]
3-Geranyl-1-(2'-methylbutanoyl) phloroglucinol (**20**)	*Hypericum natalitium* (aerial parts, ether/petroleum ether)[58] *Achyrocline alata*[59] *Esenbeckia nesiotica*[60] *Hypericum empetrifolium*[3,63] *Hypericum* spp.[64] *Hypericum roeperianum*[65] *Garcinia dauphinensis*[66] *Hypericum faberi*[67] *Hypericum jovis*[62]	–

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
3-Geranyl-1-(2'-methylpropanoyl) phloroglucinol (**21**)	*Hypericum natalitium* (aerial parts, ether/petroleum ether)[58]	–
2-Geranyloxy-1-(2-methylbutanoyl) phloroglucinol (**22**)	*Hypericum* spp. (aerial parts, acetone/CH_3OH)[64]	antimicrobial (Gram-positive bacteria)[64]
3-Geranyl-1-(3-methylbutanoyl)-phloroglucinol (**23**)	*Esenbeckia nesiotica* (aerial parts, hexane)[60]	–
3-Geranyl-1-(2'-methylbutanoyl) phloroglucinol (**24**)	*Hypericum natalitium* (aerial parts, ether/petroleum ether)[58]	–
Olympicin C (**25**)	*Hypericum olympicum* (aerial parts, hexane/CH_2Cl_2/CH_3OH)[69]	antimicrobial (*Staphylococcus aureus*)[69]
Olympicin D (**26**)	*Hypericum olympicum* (aerial parts, hexane/CH_2Cl_2/CH_3OH)[69]	antimicrobial (*Staphylococcus aureus*)[69]
Olympicin E (**27**)	*Hypericum olympicum* (aerial parts, hexane/CH_2Cl_2/CH_3OH)[69]	antimicrobial (*Staphylococcus aureus*)[69]
Hyperjovinol A (**28**)	*Hypericum jovis*[45] (aerial parts, cyclohexane)[62] *Garcinia dauphinensis*[66]	anti-inflammatory (microvascular and endothelial cells)[62]
Empetrikathiforin (**29**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	antiproliferative (microvascular and endothelial cells)[3]
1-Butanone-3-(3-methylbut-2-enylacetate)-phloroglucinol (**30**)	*Helichrysum niveum* (aerial parts, CH_3OH)[42]	–
Dauphinol F (**31**)	*Garcinia dauphinensis* (roots, CH_3CH_2OH)[66] *Hypericum jovis*[62]	–
Dauphinol E (**32**)	*Garcinia dauphinensis* (roots, CH_3CH_2OH)[66]	–
Dauphinol C (**33**)	*Garcinia dauphinensis* (roots, CH_3CH_2OH)[66]	cytotoxic (A2870)[66]
Dauphinol D (hyperannulatin B) (**34**)	*Garcinia dauphinensis* (roots, CH_3CH_2OH)[66] *Hypericum annulatum*[35]	cytotoxic (*Plasmodium falciparum*)[66]
Caespitate (**35**)	*Helichrysum caespititium* (shoots, acetone)[9] *Helichrysum niveum*[42]	–
6-Demethylacronylin (**36**)	*Acronychia laurifolia*[70]	–
Caespitin (**37**)	*Helichrysum caespititium* (whole plant, ethyl acetate)[71]	antimicrobial (*Staphylococcus aureus*; *Streptococcus pyogenes*; *Cryptococcus neoformans*; *Trichophyton rubrum*; *Trichophyton mentagrophytes*; *Microsporum canis*)[71]
(2,4,6-Trihydroxy-3-(3-methylbut-2-en-1-yl) phenyl)prop-2-en-1-one (**38**)	*Helichrysum argyrolepis* (aerial parts, ether/petroleum ether)[72]	–
3'-(3,3-Dimethylallyl)-2',4',6'-trihydroxy-7,8-dihydrochalkon (**39**)	*Helichrysum argyrolepis* (aerial parts, ether/petroleum ether)[72]	–
1-(2',4'-Dihydroxy-6'-(3''-methyl-2''-butenyloxy)-5'-(3''-methyl-2''-butenyl))phenylethanone (**40**)	*Euodia lunu-ankenda* (roots, CH_2Cl_2/CH_3OH)[73]	–
Olympicin A (**41**)	*Hypericum olympicum* (aerial parts, hexane/CH_2Cl_2/CH_3OH)[69]	antimicrobial (*Staphylococcus aureus*)[69]
Melicopol (**42**)	*Melicope broadbentiana* (bark, ether/petroleum ether/CH_3OH)[33]	–
1-(2',4'-Dihydroxy-6'-(3'',7''-dimethylocta-2'',6''-dienyloxy)-5'-(3''-methyl-2''-butenyl)) phenylethanone (**43**)	*Euodia lunu-ankenda* (roots, CH_2Cl_2/CH_3OH)[73]	–
3-Farnesyl-2,4,6-trihydroxyacetophenone (**44**)	*Boronza ramose* (aerial parts, petroleum ether/ethyl acetate/CH_3OH)[48]	–
Olympicin B (**45**)	*Hypericum olympicum* (aerial parts, hexane/CH_2Cl_2/CH_3OH)[69]	antimicrobial (*Staphylococcus aureus*)[69]
Hyperfaberol E (**46**)	*Hypericum faberi* (whole plant, CH_3OH)[74]	cytotoxic (ECA-109 and PANC-1)[74]

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
Hyperfaberol C (**47**)	*Hypericum faberi* (whole plant, CH_3OH)[74]	cytotoxic (ECA-109 and PANC-1)[74]
Iso-hyperjovinol-A (**48**)	*Hypericum jovis* (aerial parts, CH_2Cl_2/CH_3OH)[62]	anti-inflammatory (microvascular and endothelial cells)[62]
Hyperfaberol D (**49**)	*Hypericum faberi* (whole plant, CH_3OH)[74]	cytotoxic (ECA-109 and PANC-1)[74]
3'-Methyl-isohyperjovinol A (**50**)	*Hypericum jovis* (aerial parts, cyclohexane)[62]	–
Crassipetalonol A (**51**)	*Acronychia crassipetala* (fruits, hexane/$CH_2Cl_2/CH_3OH/H_2O$)[75]	antimicrobial (*Staphylococcus aureus*)[75]
Crassipetalone A (**52**)	*Acronychia crassipetala* (fruits, hexane/$CH_2Cl_2/CH_3OH/H_2O$)[75]	antimicrobial (*Staphylococcus aureus*)[75]
Acronyculatin S (**53**)	*Mallotus oppositifolius* (leaves, CH_2Cl_2/CH_3OH)[76]	antimicrobial (*Escherichia coli*, *Staphylococcus aureus*; *Salmonella paratyphi*; *Pseudomonas aeruginosa*)[76]
2,6-Dihydroxy-4-geranyloxy-3-prenylacetophenone (**54**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[46] *Melicope obtusifolia*[47]	–
Otogirin (**55**)	*Hypericum erectum* (whole plant, hexane)[77-79] *Hypericum faberi*[74]	antimicrobial (*Staphylococcus aureus*; *Bacillus subtilis*)[78,79]
4-Geranyloxy-3-prenyl-2,6,β-trihydroxyacetophenone (**56**)	*Evodia merrillii* (fruits, CH_3CH_2OH/H_2O)[56] *Melicope obtusifolia*[47]	–
Hyperannulatin A (**57**)	*Hypericum annulatum* (aerial parts, hexane)[35]	cytotoxic (HL-60, HL-60/Dox, MDA-MB, SKW-3 and K-562)[35]
1-(3,5-Dihydroxy-1-((3-methylbut-2-enyl)oxy) phenyl)-2-methyl-1-methylbutan-1-one (**58**)	*Hypericum calycinum* (aerial parts, petroleum ether)[40]	antifungal and antimalarial (*Cladosporium cucumerinum*; *Plasmodium falciparum*)[40]
Adotogirin (**59**)	*Hypericum erectum* (roots, CH_3OH)[79]	antimicrobial (*Staphylococcus aureus*; *Bacillus subtilis*)[79]
Empetrifelixin D (**60**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
Empetrifelixin C (**61**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
Prereminol (**62**)	*Remirea maritima* (rhizome, $CHCl_3$)[49]	–
Empetrifelixin A (**63**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
Empetrifelixin B (**64**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
Prenylacronylin (**65**)	*Acronychia pedunculata* (root bark, CH_2Cl_2)[50,51,80-84] *Euodia lunu-ankenda*[73] *Acronychia trifoliolata*[53]	–
Laricifolin B (**66**)	*Hypericum laricifolium* (aerial parts, hexane)[85]	–
Laricifolin A (**67**)	*Hypericum laricifolium* (aerial parts, hexane)[85]	–
2,4,6-Trihydroxy-1-(2'-methyl-butanoyl)-3-(2'',3''-epoxy-3''-methyl-butyl)-5-(3'''-methyl-2'''-butenyl)-benzene (**68**)	*Hypericum foliosum* (aerial parts, hexane/$CHCl_3/CH_3OH$)[86]	antimicrobial (*Staphylococcus aureus*)[86]
4,6-Dihydroxy-1- ethanoyl-2-methoxy-3-(3''- methyl-but-2''-enyl)-5-(3'''-methyl-2'''-butanoyl)-) benzene (**69**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[87]	–
Acronyculatin R (**70**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[88]	cytotoxic (MCF-7)[88]

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
4,6-Dihydroxy-1- ethanoyl-2-methoxy-3-(3''- methyl-but-2''-enyl)-5-(3''-methyl-but-1''-enyl)-) benzene (**71**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[87]	cytotoxic (MCF-7)[87]
Acronyculatin F (**72**)	*Acronychia pedunculata* (leaves, CH_3OH)[83]	inhibitory mammalian DNA polymerases and human cancer cell growth[83]
1-(4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3''-hydroxy-3''-methyl-but-1''-enoyl)-5-(3''-methyl-but-2''-enyl))benzene (**73**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[87]	cytotoxic (MCF-7)[87]
Empetrikajaforin (**74**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[3]	–
Acronyculatin Q (**75**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[88]	cytotoxic (MCF-7)[88]
4,6-Dihydroxy-1- ethanoyl-2-methoxy-3-(3''- methyl-but-2''-enyl)-5-(3'''-hydroxy-3'''-methyl-but-1'''-enyl)-benzene (**76**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[87]	–
4,6-Dihydroxy-1- ethanoyl-2-methoxy-3-(3''- methyl-but-2''-enyl)-5-(3'''-methyl-but-1'''-enyl)-benzene (**77**)	*Acronychia oligophlebia* (leaves, CH_3CH_2OH/H_2O)[87]	–
Hyperjaponol J (**78**)	*Hypericum japonicum* (whole plant, CH_3CH_2OH/H_2O)[68]	cytotoxic (HT22)[68]
Hyperjaponol K (**79**)	*Hypericum japonicum* (whole plant, CH_3CH_2OH/H_2O)[68]	cytotoxic (HT22)[68]
2-Acetyl-3,5-dihydroxy-1-geranoxy-6-methyl-4-(2-methyl)-butyryl-benzene (**80**)	*Hypericum japonicum* (whole plant, hexane)[89]	–
Acronyculatin A (**81**)	*Acronychia pedunculata* (stems and roots, CH_3OH)[90] *Acronychia pubescens*[54]	–
1-Acetyl-4-isopentenyl-6-methylphloroglucinol (**82**)	*Leucanthemopsis pulverulenta* (roots, CH_3CH_2OH)[91]	–
1-Acetyl-3-hydroxy-2,6-dimethyl-4-isopentenylphloroglucinol (**83**)	*Leucanthemopsis pulverulenta* (roots, CH_3CH_2OH)[91]	–
Melibarbinon B (**84**)	*Melicope barbigera* (leaves, CH_2Cl_2)[92]	–
2,4-Dihydroxy-3,6-dimethoxy-5-(3',3'-dimethylallyl)-butyrophenone (**85**)	*Leontonyx spathulatus* (aerial parts, ether/petroleum ether)[41]	–
Acronyculatin P (**86**)	*Acronychia pedunculata* (Stem Bark, CH_3OH)[85]	–
1'-(2,4-Dihydroxy-3-(3''-methylbut-2''-enyl)-5-(1'''-ethoxy-3'''-methylbutyl)-6'-methoxy)-phenylethanone (**87**)	*Acronychia pedunculata* (leaves, CH_2Cl_2)[83]	–
Acronyculatin C (**88**)	*Acronychia pedunculata* (stems and roots, CH_3OH)[90]	–
2β-Isopropyl-3β-methyl-8-(3',3'-dimethylallyl)-5,7-dihydroxychroman-4-one (**89**)	*Helichrysum bellum* (aerial parts, petroleum ether)[58]	–
((2*R*,3*R*)-5,7-Dihydroxy-2,3-dimethyl-6-(3-methyl-but-2-en-1-yl)-chroman-4-one (**90**)	*Hypericum lissophloeus* (aerial parts, CH_2Cl_2)[93]	GABA-induced current stimulator[93]
2β-Isopropyl-3α-methyl-8-(3',3'-dimethylallyl)-5,7-dihydroxychroman-4-one (**91**)	*Helichrysum bellum* (aerial parts, petroleum ether)[58]	–
5,7-Dihydroxy-2-isopropyl-8-prenylchromone (**92**)	*Humulus lupulus* (female inflorescences, CH_3CH_2OH/H_2O)[94]	–
Peucenin (**93**)	*Harrisonia abyssinica* (roots, hexane)[95]	–
(±)-Japonicol F (**94**)	*Hypericum japonicum* (whole herbs, CH_3CH_2OH/H_2O)[96]	–
Madeleinol B (**95**)	*Hypericum roeperianum* (leaves, $CHCl_3/CH_3OH$)[65] *Hypericum jovis*[62]	–

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
Hyperannulatin D (**96**)	*Hypericum annulatum* (aerial parts, hexane)[35]	–
Hyperannulatin E (**97**)	*Hypericum annulatum* (aerial parts, hexane)[35]	–
Empetrikarinol A (**98**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[97]	–
Empetrikarinol B (**99**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[97] *Hypericum roeperianum*[65] *Garcinia dauphinensis*[66]	–
1-(5,7-Dihydroxy-2-methyl-2-(4-methylpent-3-enyl)-chroman-6-yl)-2-methyl-butan-1-one (**100**)	*Helichrysum bellum* (aerial parts, petroleum ether)[58] *Hypericum empetrifolium*[97] *Garcinia dauphinensis*[66]	–
1-(5,7-Dihydroxy-2-methyl-2-(4-methyl-pent-3-enyl)-chroman-8-yl)-2-methyl-butan-1-one (**101**)	*Hypericum amblycalyx* (aerial parts, petroleum ether/diethyl ether/CH_3OH/CH_3OH:H_2O)[98] *Hypericum empetrifolium*[97] *Hypericum jovis*[62]	cytotoxic (HMEC-1, KB cancer cells and Jurkat T)[62,97,98]
1-(5,7-Dihydroxy-2-methyl-2-(4-methyl-pent-3-enyl)-chroman-8-yl)-2-methyl-propan-1-one (**102**)	*Hypericum amblycalyx* (aerial parts, petroleum ether/diethyl ether/CH_3OH/CH_3OH:H_2O)[98] *Hypericum jovis*[45,62] *Hypericum empetrifolium*[97]	cytotoxic (HMEC-1, KB cancer cells and Jurkat T)[45,62,97,98]
Hypercalyxone A (**103**)	*Hypericum amblycalyx* (aerial parts, petroleum ether/diethyl ether/CH_3OH/CH_3OH:H_2O)[98] *Hypericum annulatum*[35]	cytotoxic (KB cancer cells and Jurkat T)[98]
Hypercalyxone B (**104**)	*Hypericum amblycalyx* (aerial parts, petroleum ether/diethyl ether/CH_3OH/CH_3OH:H_2O)[98]	cytotoxic (KB cancer cells and Jurkat T)[98]
Acronyculatin I (acrophenone D) (**105**)	*Acronychia trifoliolata* (Bark, CH_3OH/CH_2Cl_2)[53] *Acronychia pedunculata*[51]	cytotoxic (NCI-60)[53]
Acronyculatin K (**106**)	*Acronychia trifoliolata* (bark, CH_3OH/CH_2Cl_2)[53]	cytotoxic (NCI-60)[53]
Selwynone (**107**)	*Bosistoa selwyni* (leaves, Petroleum ether)[99]	–
Acronyculatin L (**108**) (acrophenone C)	*Acronychia trifoliolata* (bark, CH_3OH/CH_2Cl_2)[53] *Acronychia pedunculata*[100]	cytotoxic (cancer cells)[53,100]
Helicerastripyron (**109**)	*Helichrysum cerastioides* (aerial parts, ether/petroleum ether)[72]	–
1-(5,7-Dihydroxy-2-methyl-2-(4-methylpent-3-enyl)-chroman-6-yl)-2-methyl-propan-1-one (**110**)	*Hypericum jovis* (aerial parts, CH_2Cl_2/CH_3OH/H_2O)[45,62] *Hypericum empetrifolium*[97]	–
Prolificin A (**111**)	*Hypericum prolificum* (aerial parts, hexane)[101] *Hypericum* spp.[64]	cytotoxic (MCF-7, NCI-H460, SF-268, AGS and HCT-116)[101]
Petiolin J (**112**)	*Hypericum pseudopetiolatum* (aerial parts, CH_3OH)[102]	antimicrobial (*Micrococcus luteus*; *Cryptococcus neoformans*; *Trichophyton mentagrophytes*)[102]
Yojironin D (**113**)	*Hypericum yojiroanum* (whole plant, CH_3OH)[103]	–
8-Acetyl-5,7-dihydroxy-6-isopentenyl-2,2-dimethyl-2*H*-1-benzopyran (**114**)	*Melicope ptelefolia* (leaves and branches, CH_3OH)[104]	–
Empetrikarinen A (**115**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[97]	cytotoxic (HMEC-1)[97]
Empetrikarinen B (**116**)	*Hypericum empetrifolium* (aerial parts, petroleum ether)[97]	cytotoxic (HMEC-1)[97]

Table 1. Taxonomic, extraction, and biological activity data of acylphloroglucinol derivatives (cont.)

Acylphloroglucinol derivative	Species (part of the plant, extract)	Biological activity
Melibarbichromen A (**117**)	*Melicope barbigera* (leaves, CH_2Cl_2)[92]	–
Faberione E (**118**)	*Hypericum faberi* (whole plant, CH_3OH)[67]	–
Acronyculatin G (**119**)	*Acronychia pedunculata* (leaves and twigs, CH_3OH)[83] *Acronychia trifoliolata*[53]	–
Acronyculatin E (**120**)	*Acronychia pedunculata* (roots, acetone)[51,83,90] *Acronychia trifoliolata*[53]	–
Acronyculatin M (**121**)	*Acronychia trifoliolata* (bark, CH_3OH/CH_2Cl_2)[53]	–
Acrophenone E (**122**) (acronyculatin B)	*Acronychia pedunculata* (roots, acetone)[51] *Acronychia trifoliolata*[53]	–
Acronyculatin B (acronyculatin O) (**123**)	*Acronychia pedunculata* (roots, acetone)[51,90] *Acronychia trifoliolata*[53]	–
Patulinone F (**124**)	*Melicope patulinervia* (leaves, CH_3CH_2OH/H_2O)[105]	–
Harronin I (**125**)	*Harrisonia abyssinica* (fruits, CH_3OH/CH_2Cl_2)[106]	antimicrobial (*Candida albicans*; *Bacillus cereus*)[106]
Harronin II (**126**)	*Harrisonia abyssinica* (fruits, CH_3OH/CH_2Cl_2)[106]	antimicrobial (*Candida albicans*; *Bacillus cereus*)[106]
(*R*)-5-Deprenyllupulonol C (**127**)	*Humulus lupulus* (female inflorescences, CH_3CH_2OH/H_2O)[95,107]	–
(*S*)-5-Deprenyllupulonol C (**128**)	*Humulus lupulus* (female inflorescences, CH_3CH_2OH/H_2O)[95,107]	–
Patulinone G (**129**)	*Melicope patulinervia* (leaves, CH_3CH_2OH/H_2O)[105]	–
(±)-Japonicol G (**130**)	*Hypericum japonicum* (whole herbs, CH_3CH_2OH/H_2O)[96]	–
Acrophenone F (**131**)	*Acronychia pedunculata* (roots, acetone)[51]	–
Acronyculatin H (**132**)	*Acronychia pedunculata* (leaves, CH_3OH)[83]	–
Faberione A (**133**)	*Hypericum faberi* (whole plant, CH_3OH)[67]	cytotoxic (PANC-1)[67]
Faberione B (**134**)	*Hypericum faberi* (whole plant, CH_3OH)[67]	cytotoxic (PANC-1)[67]
Faberione C (**135**)	*Hypericum faberi* (whole plant, CH_3OH)[67]	cytotoxic (PANC-1)[67]
Faberione D (**136**)	*Hypericum faberi* (whole plant, CH_3OH)[67]	–
Hyperannulatin C (**137**)	*Hypericum annulatum* (aerial parts, hexane)[35]	–
Atrovirisidone (**138**)	*Garcinia atroviridis* (roots, CH_3OH)[108]	cytotoxic (HeLa) and antimicrobial (*Bacillus cereus*; *Staphylococcus aureus*)[108]
Atrovirisidone B (**139**)	*Garcinia atroviridis* (roots, CH_3OH)[109]	cytotoxic (MCF-7, DU-145 and H-460)[109]

A2870: ovarian cancer cell line; ECA-109: human esophageal cancer cell line; PANC-1: pancreatic tumor cell line; HL-60: acute myeloid leukemia; HL-60/DOX: multi-drug resistant variant of HL-60; MDA-MB: ER-negative breast carcinoma; SKW-3: T-cell leukemia; K-562: chronic myeloid leukemia; MCF-7: human breast tumor cell line; KB: human epithelial carcinoma; Jurkat T: T lymphocyte cell line; NCI-60: human tumor cell line; NCI-H460: (ung tumor cell line; SF-268: CNS tumor cell line; AGS: stomach tumor cell line; HCT-116: colon tumor cell line; HMEC-1: human microvascular endothelial cells; HT22: neuronal cell line; HeLa: human cervical carcinoma cell line; DU-145: human prostate cell line; H-460: human lung cell line; DNA: deoxyribonucleic acid.

esters can be reduced by the presence of hydroxyl groups in the ring and by the length of the ester moiety. Consequently, the absence of these substituents is related to increased cytotoxic action.[110]

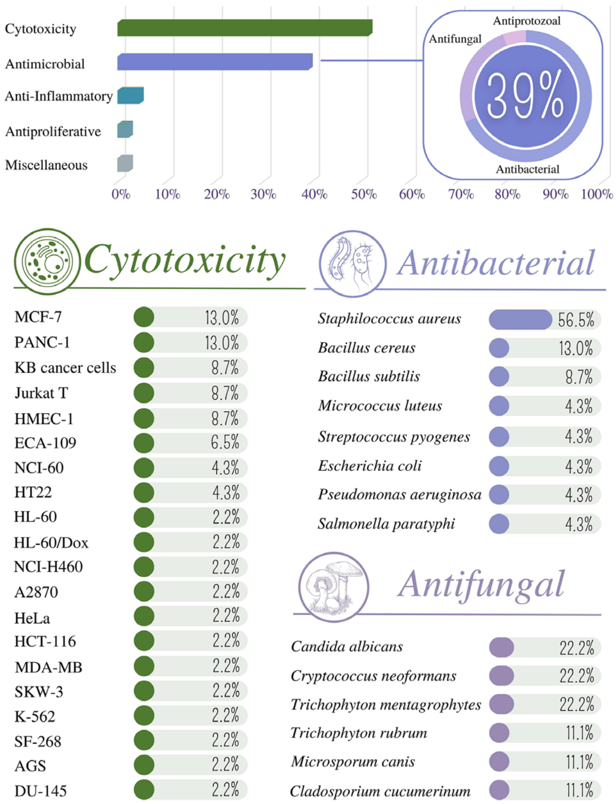


Figure 3. Biological activities associated with acylphloroglucinol derivatives.

The antimicrobial potential of a molecule is related to hydrophobicity issues and found to be enhanced by the increase of acyl and prenyl groups present in the side chains.[111,112] Monomeric acylphloroglucinols are the most related substances associated to these features. Therefore, recognizing the structural characteristics of compounds becomes important to understand the relationship between chemical structure and biological activity.

Tables 2-3 compile the data according to their nomenclature, chemical formula, taxonomic data, geographic location of specimen collection, study reference and ^{1}H and ^{13}C NMR data (chemical shifts, coupling constant, and the frequency and solvent used in research). As presented in Figure 4, these substances were mainly isolated from plants of the *Hypericum* genus.

Considering the temporary coverage of 1965-2022, experimental studies contributed by suggesting new connections between acylphloroglucinol derivatives, taxonomic species and biological activities. In this sense, spectroscopic data allowed the identification and discovery of new secondary metabolites. Allowing the construction of the phytochemical profile of the various species of interest and enriching knowledge about the elucidation of the biosynthetic pathways of the compounds of interest.

4.1. Prenylated and geranylated monocyclic acylphloroglucinol derivatives

Monomeric acylphloroglucinol derivatives are characterized by having a THB core with a conjugated acyl substituent on the benzene ring, which are further submitted to subclassification according to the substituents. This

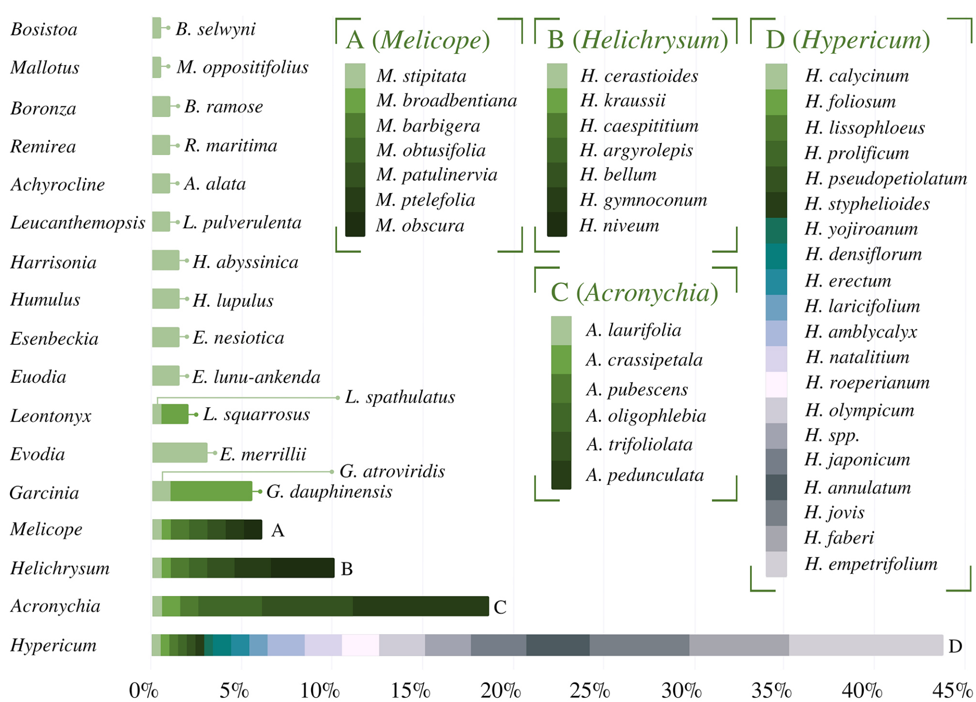


Figure 4. Summary of isolated phloroglucinols distribution according to species and genera.

review highlighted the existence of terpenes, glycosides, halogenates, prenylates and geranylates, cyclic polyketides, and substituted α-pyrone. To facilitate the analysis of the monomeric monocyclic acylphloroglucinols, they were numbered according to their structural similarity, referring to the pattern of hydrogenation of the "R" substituent groups attached to the THB core (Figure 5 and Table 2).

Compounds **1-10** are characterized by an acylated THB core with two hydroxyls and one alkoxy groups attached to the acyl group (R_1) and prenyl or geranyl at R_2. For the record, no biological activities were attributed to these derivatives (Figures 5-6; Tables 1-2).

Prenylated compounds **1-3** were isolated from extracts (diethyl ether/petroleum ether, 1:2) of the roots of the species *Leontonyx squarrosus*.[41] Associated with the genus *Helichrysum*, prenylated metabolites **4** and **5** were isolated from methanolic extracts of *H. niveum*; while geranylates **6** and **8** from root extracts in (diethyl ether/petroleum ether, 1:1) of *H. gymnoconum*.[42,58] Compounds **7** and **9** were obtained from the fruit extract of *Evodia merrillii* in 95% CH_3CH_2OH, and compound **10** was associated with aerial parts of *Boronza ramose*, extracted in sequential solvents: petroleum ether, CH_3CH_2OH and CH_3OH.[46,48]

Structures **11-35** followed the pattern of alkyl groups at R_1 and R_3, and prenyl or geranyl groups attached to the C-5 of the THB core (Figures 5 and 7; Tables 1-2).

The prenylated derivative **11** was obtained from the extraction using ethyl acetate of the roots of *Acronychia pedunculata*.[50] Compounds **12-14** were isolated in species of the genus *Helichrysum* from ethanolic and methanolic extracts of roots and aerial parts of plants of the species *H. gymnoconum* and *H. niveum*; compounds **30** and **35** were also isolated from the same genus: **30** from methanolic extracts of aerial parts of *H. niveum*, and **35** of *H. caespititium* from acetonic extracts of aerial parts of the species.[9,10,42,58] The geranylated derivatives **15** and **16** were isolated from the 95% CH_3CH_2OH extract of *Evodia merrillii* fruits.[46,56] Compound **17** was isolated from methanolic extract of the leaves of *Melicope ptelefolia*.[57] Geranylated molecules **18-22** and **24-29** were isolated from different species of *Hypericum* (*H. natalitium*, *Hypericum* spp., *H. jovis*, *H. olympicum*, and *H. empetrifolium*) and their structures were elucidated based on NMR spectroscopic data. Inherent to biological activities, **19** and **22** stand out. THB derivatives were isolated from extracts of aerial parts of *Hypericum* spp. family in an acetone/CH_3OH system, which aided in the production of biofilm by Gram-positive strains at sub-minimal inhibitory concentration (MIC) concentrations.[58,64] Derivative **23** was identified in a mixture of leaf extract in hexane of *Esenbeckia nesiotica*.[60] Phloroglucinols **25-27** of the species *H. olympicum* were isolated from the extract of the aerial parts of the plant using the solvent gradient: hexane, CH_2Cl_2 and CH_3OH; and exhibited potent MIC against multidrug-resistant *Staphylococcus* strains. In this sense, the antibacterial action of **26** stands out due to the compound containing a peroxide group in its

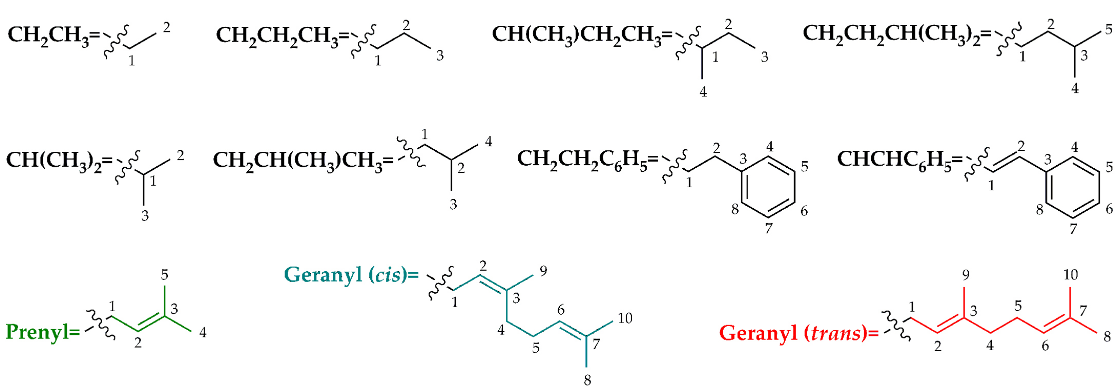


Figure 5. Standard numbering of substituents for compounds **1**-**88**.

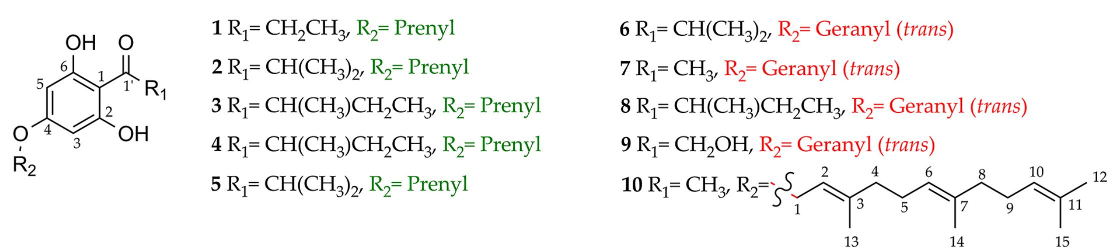


Figure 6. Monocyclic monomeric derivatives of acylphloroglucinols **1**-**10**.

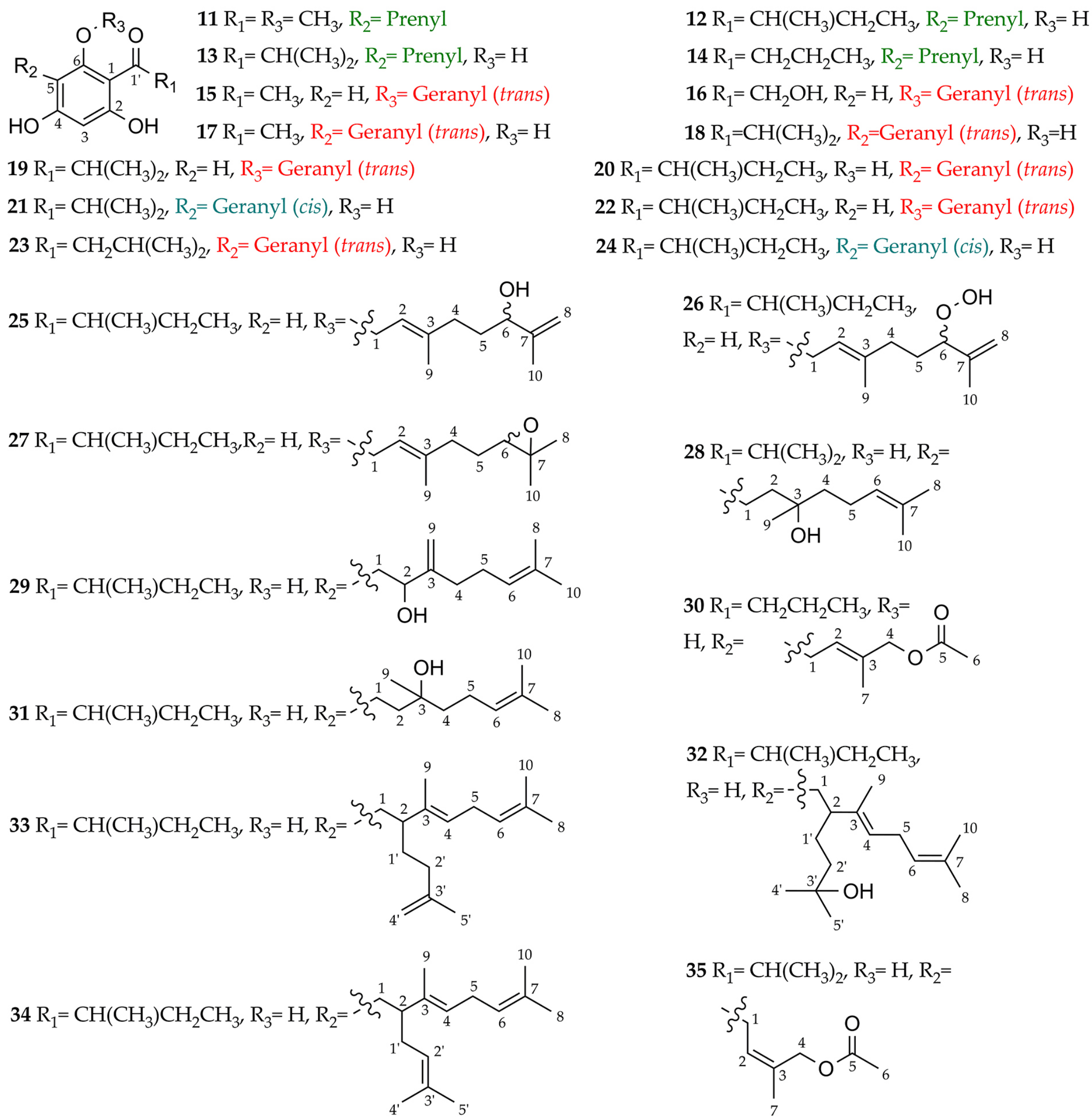


Figure 7. Monocyclic monomeric derivatives of acylphloroglucinols **11**-**35**.

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
2,4,6-Trihydroxy propiophenone-4-*O*-3'-3'dimethylallyl ether (**1**) $C_{14}H_{18}O_4$	*Leontonyx squarrosus* South Africa[41]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 5.93 (H-3 and H-5) prenyl group: δ 4.50 (H-1), 5.45 (H-2), 1.74 (H-4), and 1.81 (H-5) acyl group: δ 3.10 (H-1), and 1.18 (H-2)[41]
2,4,6-Trihydroxy isobutyrophenone-4-*O*-3',3'-dimethylallyl ether (**2**) $C_{15}H_{20}O_4$	*Leontonyx squarrosus* South Africa[41]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 10.25 (OH-2 and OH-6), and 5.95 (H-3 and H-5) prenyl group: δ 4.49 (H-1), 5.44 (H-2), 1.72 (H-4), and 1.79 (H-5) acyl group: δ 3.90 (H-1) and 1.19 (H-2 and H-3)[41]
2,4,6-Trihydroxy-2-methylbutyrophenone-4-*O*-3',3'-dimethylallyl ether (**3**) $C_{16}H_{22}O_4$	*Leontonyx squarrosus* South Africa[41] *Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 9.72 (OH-2 and OH-6) and 5.92 (H-3 and H-5) prenyl group: δ 4.49 (H-1), 5.44 (H-2), 1.79 (H-4), and 1.73 (H-5) acyl group: δ 3.70 (H-1), 1.40 (H-2), 1.84 (H-2), 0.91 (H-3), and 1.16 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.4 (C-1), 164.5 (C-2), 95.1 (C-3), 164.5 (C-4), 95.1 (C-5), and 163.1 (C-6) prenyl group: δ 65.0 (C-1), 118.6 (C-2), 139.1 (C-3), 25.8 (C-4), and 18.2 (C-5) acyl group: δ 209.9 (C-1'), 45.9 (C-1), 26.8 (C-2), 11.9 (C-3), and 16.5 (C-4)[3]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
1-(2-Methylbutanone)-4-*O*-prenyl-phloroglucinol (**4**) $C_{16}H_{22}O_4$	*Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.91 (H-3 and H-5) prenyl group: δ 4.47 (H-1), 5.42 (H-2), 1.77 (H-4), and 1.71 (H-5) acyl group: δ 3.70 (H-1), 1.38 (H-2), 0.89 (H-3), and 1.14 (H-4) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 104.5 (C-1), 164.6 (C-2, C-4, and C-6), and 95.1 (C-3 and C-5) prenyl group: δ 65.1 (C-1), 118.7 (C-2), 139.2 (C-3), 18.2 (C-4), and 25.8 (C-5) acyl group: δ 210.1 (C-1'), 45.9 (C-1), 26.9 (C-2), 16.6 (C-3), and 11.9 (C-4)[42]
1-(2-Methylpropanone)-4-*O*-prennyl-phloroglucinol (**5**) $C_{15}H_{20}O_4$	*Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.91 (H-3 and H-5) and 9.92 (OH-2 and OH-6) prenyl group: δ 4.47 (H-1), 5.42 (H-2), 1.77 (H-4), and 1.71 (H-5) acyl group: δ 3.83 (H-1) and 1.59 (H-2 and H-3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 104.0 (C-1), 164.7 (C-2, C-4, and C-6), and 95.1 (C-3 and C-5) prenyl group: δ 65.1 (C-1), 118.7 (C-2), 139.2 (C-3), 18.2 (C-4), and 25.8 (C-5) acyl group: δ 210.2 (C-1'), 39.3 (C-1), and 19.2 (C-2 and C-3)[42]
4-Geranyloxy-1-(2-methylpropanoyl)-phloroglucinol (**6**) $C_{20}H_{28}O_4$	*Helichrysum gymnoconum* South Africa[43] *Hypericum densiflorum* United States[44] *Hypericum jovis* Greece[45]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 5.96 (H-3 and H-5) and 9.2 (OH-2 and OH-6) geranyl group:[a] δ 4.51 (H-1), 5.43 (H-2), 2.09 (H-4 and H-5), 5.08 (H-6), 1.60 (H-8), 1.71 (H-9), and 1.67 (H-9)[43] ^{13}C NMR (50 MHz, $CDCl_3$) THB core: δ 104.0 (C-1), 164.7 (C-2), 94.5 (C-3 and C-5), 163.3 (C-4), and 164.7 (C-6) geranyl group:[a] δ 65.1 (C-1), 118.4 (C-2), 142.1 (C-3), 39.5 (C-4), 26.2 (C-5), 123.6 (C-6), 131.9 (C-7), 25.7 (C-8), 16.7 (C-9), and 17.7 (C-10) acyl group: δ 210.2 (C-1'), 39.2 (C-1), and 19.2 (C-2 and C-3)[45]
2,6-Dihydroxy-4-geranyloxyacetophenone (**7**) $C_{18}H_{24}O_4$	*Evodia merrillii* Taiwan[46] *Melicope obscura* Reunion Island[47]	^{1}H NMR[b] (300 MHz) THB core: δ 5.95 (H-3 and H-5) geranyl group:[a] δ 4.47 (H-1), 5.39 (H-2), 2.06 (H-4 and H-5), 5.04 (H-6), 1.56 (H-8), 1.67 (H-9), and 1.64 (H-10) acyl group: δ 2.68 (CH_3) ^{13}C NMR[b] (75 MHz) THB core: 105.2 (C-1), 163.8 (C-2), 94.7 (C-3), 165.5 (C-4), 94.7 (C-5), and 163.8 (C-6), geranyl group:[a] δ 65.1 (C-1), 118.3 (C-2), 142.2 (C-3), 39.4 (C-4), 26.2 (C-5), 123.6 (C-6), 131.8 (C-7), 17.6 (C-8), 16.5 (C-9), and 25.5 (C-10) acyl group: δ 204.1 (C-1') and 32.4 (CH_3)[46]
4-Geranyloxy-1-(2-methylbutanoyl)-phloroglucinol (**8**) $C_{21}H_{30}O_4$	*Helichrysum gymnoconum* South Africa[43] *Hypericum densiflorum* United States[44]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 5.96 (H-3 and H-5) and 9.2 (OH-2 and OH-6) geranyl group:[a] δ 4.51 (H-1), 5.43 (H-2), 2.09 (H-4 and H-5), 5.08 (H-6), 1.60 (H-8), 1.71 (H-9), and 1.67 (H-9)[43] ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 106.0 (C-1), 167.6 (C-2), 91.6 (C-3), 162.1 (C-4), 96.5 (C-5), and 162.6 (C-6) geranyl group:[a] δ 65.7 (C-1), 118.2 (C-2), 142.5 (C-3), 39.6 (C-4), 25.8 (C-5), 123.7 (C-6), 132.1 (C-7), 26.4 (C-8), 16.6 (C-9), and 17.8 (C-10) acyl group: δ 210.5 (C-1'), 46.2 (C-1), 26.9 (C-2), 12.0 (C-3), and 16.7 (C-4)[44]
4-Geranyloxy-2,6,β-trihydroxyacetophenone (**9**) $C_{18}H_{24}O_5$	*Evodia merrillii* Taiwan[46] *Melicope obscura* Reunion Island[47]	^{1}H NMR[b] (300 MHz) 4.33 (OH), and 10.45 (OH) THB core: δ 5.95 (H-3 and H-5) geranyl group:[a] δ 4.51 (H-1), 5.40 (H-2), 2.07 (H-4 and H-5), 5.06 (H-6), 1.58 (H-8), 1.70 (H-9), and 1.65 (H-10) acyl group: δ 4.81 (CH_2) ^{13}C NMR[b] (75 MHz) THB core: δ 102.5 (C-1), 163.7 (C-2), 94.8 (C-3), 166.5 (C-4), 94.8 (C-5), and 163.7 (C-6) geranyl group:[a] δ 65.3 (C-1), 118.3 (C-2), 142.4 (C-3), 39.3 (C-4), 26.2 (C-5), 123.6 (C-6), 131.9 (C-7), 17.7 (C-8), 16.7 (C-9), and 25.6 (C-10) acyl group: δ 200.7 (C-1') and 68.0 (CH_2)[46]
4-Farnesyloxy-2,6-dihydroxyacetophenone (**10**) $C_{23}H_{32}O_4$	*Boronza ramose* Australia[48]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.95 (H-3 and H-5) R_4 group: δ 4.52 (H-1), 5.44 (H-2), 1.94-2.16 (H-4, H-5, H-8, and H-9), 5.09 (H-6), 5.09 (H-10), 1.68 (H-12), 1.73 (H-13), 1.60 (H-14), and 1.60 (H-15) acyl group: δ 2.69 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 105.3 (C-1), 163.6 (C-2 and C-6), 95.0 (C-3 and C-5), and 165.4 (C-4) R_4 group: δ 65.4 (C-1), 118.6 (C-2), 142.5 (C-3), 39.7 (C-4), 26.3 (C-5), 123.7 (C-6), 135.8 (C-7), 39.9 (C-8), 26.9 (C-9), 124.5 (C-10), 131.6 (C-11), 25.9 (C-12), 16.9 (C-13), 16.2 (C-14), and 17.9 (C-15) acyl group: δ 203.7 (C-1') and 32.9 (CH_3)[48]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, *δ* / ppm)
Acronylin (**11**) $C_{14}H_{18}O_4$	*Remirea maritima*[c] [49] *Acronychia pedunculata* Sri Lanka[50] Taiwan[51] *Melicope stipitata* Australia[52] *Acronychia trifoliolata* Indonesia[53] *Acronychia pubescens* Australia[54]	NMR data not found
1-(2-Methylbutanone)- 3-prenylphloroglucinol (**12**) $C_{16}H_{22}O_4$	*Helichrysum gymnoconum* South Africa[43] *Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: *δ* 5.83 (H-3), 8.81(OH-4), and 11.76 (OH-6) prenyl group: *δ* 3.32 (H-1), 5.21 (H-2), 1.73 (H-4), and 1.78 (H-5) acyl group: *δ* 3.74 (H-1), 1.37 (H-2), 0.88 (H-3), and 1.13 (H-4) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: *δ* 105.7 (C-1), 160.7 (C-2), 95.4 (C-3), 159.9 (C-4), 104.7 (C-5), and 162.6 (C-6) prenyl group: *δ* 21.6 (C-1), 121.6 (C-2), 135.9 (C-3), 25.8 (C-4), and 17.9 (C-5) acyl group: *δ* 210.8 (C-1'), 45.9 (C-1), 26.9 (C-2), 11.9 (C-3), and 16.9 (C-4)[42]
1-(2-Methylpropanone)- 3-prenylphloroglucinol (**13**) $C_{15}H_{20}O_4$	*Helichrysum gymnoconum* South Africa[10,43] *Helichrysum kraussii* South Africa[55] *Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, CD_3COCD_3) THB core: *δ* 6.06 (H-3), 9.33 (OH-4), and 14.09 (OH-6) prenyl group: *δ* 3.23 (H-1), 5.21 (H-2), 1.73 (H-4), and 1.62 (H-5) acyl group: *δ* 3.98 (H-1) and 1.12 (H-2 and H-3) ^{13}C NMR (100 MHz, CD_3COCD_3) THB core: *δ* 104.3 (C-1), 160.1 (C-2), 95.1 (C-3), 162.5 (C-4), 108.0 (C-5), and 165.2 (C-6) prenyl group: *δ* 22.1 (C-1), 124.2 (C-2), 130.8 (C-3), 17.9 (C-4), and 25.9 (C-5) acyl group: *δ* 210.9 (C-1'), 39.7 (C-1), and 19.8 (C-2 and C-3)[42]
1-(Butanone)-3-prenyl-phloroglucinol (**14**) $C_{15}H_{20}O_4$	*Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, CD_3COCD_3) THB core: *δ* 6.05 (H-3), 9.31 (OH-4), and 14.1 (OH-6) prenyl group: *δ* 3.22 (H-1), 5.20 (H-2), 1.61 (H-4), and 1.72 (H-5) acyl group: *δ* 3.04 (H-1), 1.67 (H-2), and 0.94 (H-3) ^{13}C NMR (100 MHz, CD_3COCD_3) THB core: *δ* 105.1 (C-1), 162.6 (C-2), 95.0 (C-3), 160.5 (C-4), 107.9 (C-5), and 165.2 (C-6) prenyl group: *δ* 22.0 (C-1), 124.3 (C-2), 130.8 (C-3), 26.0 (C-4), and 17.9 (C-5) acyl group: *δ* 206.5 (C-1'), 46.5 (C-1), 19.0 (C-2), and 14.4 (C-3)[42]
2-(1'-Geranyloxy)- 4,6-dihydroxyacetophenone (**15**) $C_{18}H_{24}O_4$	*Evodia merrillii* Taiwan[46]	^{1}H NMR[b] (300 MHz) THB core: *δ* 5.96 (H-3), 5.90 (H-5), 6.17 (OH-2 or OH-4), and 13.96 (OH-2 or OH-4) geranyl group:[a] *δ* 4.54 (H-1), 5.48 (H-2), 2.09 (H-4 and H-5), 5.06 (H-6), 1.59 (H-8), 1.72 (H-9), and 1.66 (H-10) acyl group: *δ* 2.60 (CH_3) ^{13}C NMR[b] (75 MHz) THB core: *δ* 106.4 (C-1), 167.2 (C-2), 96.3 (C-3), 163.1 (C-4), 91.6 (C-5), and 162.7 (C-6) geranyl group:[a] *δ* 65.7 (C-1), 118.4 (C-2), 142.2 (C-3), 39.4 (C-4), 26.2 (C-5), 123.6 (C-6), 132.0 (C-7), 17.7 (C-8), 16.6 (C-9), and 25.6 (C-10) acyl group: *δ* 203.5 (C-1') and 33.0 (CH_3)[46]
2-(1'-Geranyloxy)- 4,6,β-trihydroxyacetophenone (**16**) $C_{18}H_{24}O_5$	*Evodia merrillii* Taiwan[56]	^{1}H NMR[d] ($CDCl_3$) *δ* 3.89 (OH), 6.27 (OH), and 13.09 (OH) THB core: *δ* 5.90 (H-3) and 6.00 (H-5) geranyl group:[a] *δ* 4.56 (H-1), 5.48 (H-2), 2.10 (H-4 and H-5), 5.07 (H-6), 1.59 (H-8), 1.72 (H-9), and 1.67 (H-10) acyl group: *δ* 4.71 (CH_2) ^{13}C NMR[d] ($CDCl_3$) THB core: *δ* 103.7 (C-1), 166.9 (C-2), 96.5 (C-3), 163.9 (C-4), 91.8 (C-5), and 163.4 (C-6) geranyl group:[a] *δ* 65.9 (C-1), 117.8 (C-2), 143.0 (C-3), 39.5 (C-4), 26.3 (C-5), 123.5 (C-6), 132.1 (C-7), 17.7 (C-8), 16.6 (C-9), and 25.6 (C-10) acyl group: *δ* 201.7 (C-1') and 68.6 (CH_2)[56]
2,4,6-Trihydroxy-3-geranyl- acetophenone (**17**) $C_{18}H_{24}O_4$	*Melicope ptelefolia* Malaysia[57]	^{1}H NMR (500 MHz, CD_3OD) THB core: *δ* 5.92 (H-3) geranyl group:[a] *δ* 3.21 (H-1), 5.20 (H-2), 1.96 (H-4), 2.06 (H-5), 5.08 (H-6), 1.63 (H-8), 1.76 (H-9), and 1.58 (H-10) acyl group: *δ* 2.64 (CH_3) ^{13}C NMR (125 MHz, CD_3OD) THB core: *δ* 104.3 (C-1), 160.7 (C-2), 93.6 (C-3), 162.8 (C-4), 106.8 (C-5), and 163.7 (C-6) geranyl group:[a] *δ* 20.9 (C-1), 123.5 (C-2), 133.5 (C-3), 39.8 (C-4), 26.6 (C-5), 124.4 (C-6), 130.8 (C-7), 24.7 (C-8), 15.0 (C-9), and 16.6 (C-10) acyl group: *δ* 203.4 (C-1') and 31.7 (CH_3)[57]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
3-Geranyl-1-(2'-methylpropanoyl) phloroglucinol (**18**) $C_{20}H_{28}O_4$	*Hypericum natalitium* South Africa[58] *Achyrocline alata* Brazil[59] *Esenbeckia nesiotica* Mexico[60] *Hypericum styphelioides* Cuba[61] *Hypericum jovis* Greece[45,62] *Hypericum empetrifolium* Austria[63] Greece[3] *Hypericum* spp. United States[64] *Hypericum roeperianum* Cameroon[65] *Garcinia dauphinensis* Madagascar[66] *Hypericum annulatum* Rhodopi Mountain[35] *Hypericum faberi* China[67] *Hypericum japonicum* China[68]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 8.31 (OH-2), 5.97 (OH-4), 11.60 (OH-6), and 5.83 (H-3) geranyl group:[a] δ 3.38 (H-1), 5.26 (H-2), 2.09 (H-4), 2.11 (H-5), 5.05 (H-6), 1.67 (H-8), 1.81 (H-9), and 1.59 (H-10) acyl group: δ 3.87 (H-1) and 1.17 (H-2 and H-3) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.1 (C-1), 159.9 (C-2), 95.4 (C-3), 160.6 (C-4), 105.6 (C-5), and 162.6 (C-6) geranyl group:[a] δ 21.6 (C-1), 121.4 (C-2), 140.1 (C-3), 39.6 (C-4), 26.2 (C-5), 123.5 (C-6), 132.1 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.6 (C-10) acyl group: δ 210.5 (C-1'), 39.2 (C-1), and 19.2 (C-2 and C-3)[3]
2-Geranyloxy-1-(2-methylpropanoyl) phloroglucinol (**19**) $C_{20}H_{28}O_4$	*Hypericum* spp. United States[64]	NMR data not found
3-Geranyl-1-(2'-methylbutanoyl) phloroglucinol (**20**) $C_{21}H_{30}O_4$	*Hypericum natalitium* South Africa[58] *Achyrocline alata* Brazil[59] *Esenbeckia nesiotica* Mexico[60] *Hypericum empetrifolium* Austria[63] Greece[3] *Hypericum* spp. United States[64] *Hypericum roeperianum* Cameroon[65] *Garcinia dauphinensis* Madagascar[66] *Hypericum faberi* China[67] *Hypericum jovis* Greece[62]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 8.20 (OH-2), 5.96 (OH-4), 11.75 (OH-6), and 5.82 (H-3) geranyl group:[a] δ 3.38 (H-1), 5.26 (H-2), 2.09 (H-4), 2.11 (H-5), 5.05 (H-6), 1.68 (H-8), 1.82 (H-9), and 1.60 (H-10) acyl group: δ 3.74 (H-1), 1.40 (H-2), 1.83 (H-2), 0.90 (H-3), and 1.16 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.8 (C-1), 159.9 (C-2), 95.4 (C-3), 160.7 (C-4), 105.6 (C-5), and 162.6 (C-6) geranyl group:[a] δ 21.6 (C-1), 121.4 (C-2), 140.1 (C-3), 39.6 (C-4), 26.2 (C-5), 123.5 (C-6), 132.1 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.7 (C-10) acyl group: δ 210.3 (C-1'), 45.9 (C-1), 26.9 (C-2), 11.9 (C-3), and 16.6 (C-4)[3]
3-Geranyl-1-(2'-methylpropanoyl) phloroglucinol (**21**) $C_{20}H_{28}O_4$	*Hypericum natalitium* South Africa[58]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 5.88 (H-5) geranyl group:[e] δ 3.37 (H-1), 5.18 (H-2), 2.26 (H-4), 2.16 (H-5), 5.24 (H-6), 1.63 (H-8), 1.81 (H-9), and 1.70 (H-10)[58]
2-Geranyloxy-1-(2-methylbutanoyl) phloroglucinol (**22**) $C_{21}H_{30}O_4$	*Hypericum* spp. United States[64]	NMR data not found
3-Geranyl-1-(3-methylbutanoyl)-phloroglucinol (**23**) $C_{21}H_{30}O_4$	*Esenbeckia nesiotica* Mexico[60]	^{1}H NMR (300 MHz, $CDCl_3$) THB core: δ 5.82 (H-3), 8.50 (OH-2), 6.08 (OH-4), and 11.62 (C-6) geranyl group:[a] δ 3.39 (H-1), 5.24 (H-2), 2.10 (H-4 and H-5), 5.06 (H-6), 1.68 (H-8), 1.59 (H-9), and 1.81 (H-10) acyl group: δ 2.94 (H-1), 2.26 (H-2), and 0.97 (H-3 and H-4)[60]
3-Geranyl-1-(2'-methylbutanoyl) phloroglucinol (**24**) $C_{21}H_{30}O_4$	*Hypericum natalitium* South Africa[58]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 5.88 (H-5) geranyl group:[e] δ 3.37 (H-1), 5.18 (H-2), 2.26 (H-4), 2.16 (H-5), 5.24 (H-6), 1.63 (H-8), 1.81 (H-9), and 1.70 (H-10)[58]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
Olympicin C (**25**) $C_{21}H_{30}O_5$	*Hypericum olympicum* England[69]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 5.92 (H-3), 5.98 (H-5), and 13.99 (OH-6) R_2 group: δ 4.57 (H-1), 5.53 (H-2), 2.15 (H-4), 1.75 (H-5), 4.08 (H-6), 4.95 (H-8), 4.87 (H-8), 1.74 (H-9), and 1.76 (H-10) acyl group: δ 3.64 (H-1), 1.37 (H-2), 1.80 (H-2), 0.88 (H-3), and 1.12 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.9 (C-1), 162.4 (C-2), 91.6 (C-3), 161.9 (C-4), 96.6 (C-5), and 167.6 (C-6) R_2 group: δ 65.6 (C-1), 118.7 (C-2), 141.9 (C-3), 35.5 (C-4), 26.8 (C-5), 75.5 (C-6), 147.2 (C-7), 111.4 (C-8), 17.6 (C-9), and 16.7 (C-10) acyl group: δ 210.3 (C-1'), 46.1 (C-1), 26.8 (C-2), 11.9 (C-3), and 16.7 (C-4)[69]
Olympicin D (**26**) $C_{21}H_{30}O_6$	*Hypericum olympicum* England[69]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 5.91 (H-3), 5.98 (H-5), 5.32 (OH-4), and 13.99 (OH-6) R_2 group: δ 4.58 (H-1), 5.52 (H-2), 2.21 (H-4), 1.75 (H-5), 4.32 (H-6), 5.02 (H-8), 5.05 (H-8), and 1.75 (H-9 and H-10) acyl group: δ 3.63 (H-1), 1.35 (H-2), 1.80 (H-2), 0.88 (H-3), and 1.11 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.9 (C-1), 162.4 (C-2), 91.7 (C-3), 162.0 (C-4), 96.6 (C-5), and 167.5 (C-6) R_2 group: δ 65.6 (C-1), 119.2 (C-2), 141.2 (C-3), 35.2 (C-4), 26.8 (C-5), 89.0 (C-6), 143.3 (C-7), 114.6 (C-8), 16.6 (C-9), and 17.2 (C-10) acyl group: δ 210.3 (C-1'), 46.1 (C-1), 26.8 (C-2), 11.9 (C-3), and 16.6 (C-4)[69]
Olympicin E (**27**) $C_{21}H_{30}O_5$	*Hypericum olympicum* England[69]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 6.02 (H-3), 5.98 (H-5), 6.90 (OH-4), and 13.95 (OH-6) R_2 group: δ 4.67 (H-1), 5.50 (H-2), 2.30 (H-4), 1.65 (H-5), 1.90 (H-5), 2.77 (H-6), 1.31 (H-8), 1.76 (H-9), and 1.34 (H-10) acyl group: δ 3.63 (H-1), 1.38 (H-2), 1.81 (H-2), 0.90 (H-3), and 1.10 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.5 (C-1), 162.3 (C-2), 92.7 (C-3), 162.8 (C-4), 96.8 (C-5), and 167.6 (C-6) R_2 group: δ 66.4 (C-1), 121.9 (C-2), 138.5 (C-3), 37.0 (C-4), 26.5 (C-5), 65.1 (C-6), 59.1 (C-7), 18.9 (C-8), 16.0 (C-9), and 24.6 (C-10) acyl group: δ 210.0 (C-1'), 46.1 (C-1), 26.5 (C-2), 12.0 (C-3), and 16.6 (C-4)[69]
Hyperjovinol A (**28**) $C_{20}H_{30}O_5$	*Hypericum jovis* Greece[45,62] *Garcinia dauphinensis* Madagascar[66]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.85 (H-3) R_5 group: δ 2.60 (H-1), 2.65 (H-1), 1.73 (H-2), 1.55 (H-4), 2.03 (H-5), 5.08 (H-6), 1.65 (H-8), 1.22 (H-9), and 1.58 (H-10) acyl group: δ 3.90 (H-2) and 1.14 (H-3 and H-4) ^{13}C NMR (50 MHz, $CDCl_3$) THB core: δ 104.1 (C-1), 159.6 (C-2), 95.4 (C-3), 160.6 (C-4), 108.7 (C-5), and 162.8 (C-6) R_5 group: δ 15.9 (C-1), 39.7 (C-2), 74.8 (C-3), 41.9 (C-4), 22.9 (C-5), 123.9 (C-6), 132.5 (C-7), 25.7 (C-8), 26.6 (C-9), and 17.6 (C-10) acyl group: δ 210.9 (C-1'), 39.1 (C-1), and 19.3 (C-2 and C-3)[45]
Empetrikathiforin (**29**) $C_{21}H_{30}O_5$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 5.86 (H-3), 7.73 (OH-2), 7.73 (OH-4), and 12.55 (OH-6) R_5 group: δ 2.69 (H-1), 3.11 (H-1), 4.35 (H-2), 2.45 (OH-2), 2.13 (H-4), 2.21 (H-4), 2.18 (H-5), 5.14 (H-6), 1.69 (H-8), 4.91 (H-9), 5.06 (H-9), and 1.62 (H-10) acyl group: δ 3.77 (H-1), 1.40 (H-2), 1.83 (H-2), 0.91 (H-3), and 1.16 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.8 (C-1), 160.3 (C-2), 95.5 (C-3), 161.7 (C-4), 105.5 (C-5), and 163.5 (C-6) R_5 group: δ 29.1 (C-1), 77.3 (C-2), 151.0 (C-3), 32.1 (C-4), 26.4 (C-5), 123.7 (C-6), 132.2 (C-7), 25.6 (C-8), 109.2 (C-9), and 17.7 (C-10) acyl group: δ 210.4 (C-1'), 45.9 (C-1), 26.9 (C-2), 11.9 (C-3), and 16.6 (C-4)[3]
1-Butanone-3-(3-methylbut-2-enylacetate)-phloroglucinol (**30**) $C_{17}H_{22}O_6$	*Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, CD_3COCD_3) THB core: δ 9.25 (OH-2), 9.66 (OH-4), and 14.0 (OH-6) R_5 group: δ 3.45 (H-1), 5.51 (H-2), 4.82 (H-4), 2.07 (H-6), and 1.71 (H-7) acyl group: δ 3.08 (H-1), 1.71 (H-2), and 0.99 (H-3) ^{13}C NMR (100 MHz, CD_3COCD_3) THB core: δ 105.4 (C-1), 161.1 (C-2), 95.3 (C-3), 162.8 (C-4), 107.0 (C-5), and 165.4 (C-6) R_5 group: δ 22.1 (C-1), 129.6 (C-2), 130.4 (C-3), 64.0 (C-4), 171.5 (C-5), 21.1 (C-6), and 21.8 (C-7) acyl group: δ 206.9 (C-1'), 46.8 (C-1), 19.2 (C-2), and 14.6 (C-3)[42]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
Dauphinol F (**31**) $C_{21}H_{32}O_5$	*Garcinia dauphinensis* Madagascar[66] *Hypericum jovis* Greece[62]	^{1}H NMR[d] ($CDCl_3$) THB core: δ 5.84 (H-3), 7.54 (OH), and 12.46 (OH) R_5 group: δ 2.67 (H-1), 1.75 (H-2), 1.57 (H-4), 2.06 (H-5), 5.12 (H-6), 1.69 (H-8), 1.62 (H-9), and 1.24 (H-10) acyl group: δ 3.77 (H-1), 1.83 (H-2), 1.39 (H-2), 0.91 (H-3), and 1.16 (H-4) ^{13}C NMR[d] ($CDCl_3$) THB core: δ 95.8 (C-3) R_5 group: δ 15.9 (C-1), 39.9 (C-2), 74.9 (C-3), 42.1 (C-4), 23.1 (C-5), 124.0 (C-6), 132.9 (C-7), 17.9 (C-8), 26.9 (C-9), and 25.9 (C-10) acyl group: δ 46.0 (C-1), 27.1 (C-2), 12.1 (C-3), and 16.9 (C-4)[66]
Dauphinol E (**32**) $C_{26}H_{40}O_5$	*Garcinia dauphinensis* Madagascar[66]	^{1}H NMR[d] ($CDCl_3$) THB core: δ 5.80 (H-3) and 1.64 (OH) R_5 group: δ 2.66 (H-1), 2.57 (H-1), 2.86 (H-2), 5.16 (H-4), 2.56 (H-5), 2.38 (H-5), 4.80 (H-6), 1.52 (H-8), 1.69 (H-9), 1.61 (H-10), 1.52 (H-1'), 1.35 (H-2'), 1.22 (H-4'), and 1.23 (H-5') acyl group: δ 3.72 (H-1), 1.82 (H-2), 1.39 (H-2), 0.90 (H-3), and 1.15 (H-4) ^{13}C NMR[d] ($CDCl_3$) THB core: δ 106.7 (C-1), 160.0 (C-2), 95.4 (C-3), 160.0 (C-4), and 104.0 (C-5) R_5 group: δ 26.7 (C-1), 39.4 (C-2), 136.0 (C-3), 127.6 (C-4), 26.7 (C-5), 123.7 (C-6), 131.2 (C-7), 18.0 (C-8), 18.8 (C-9), 26.1 (C-10), 29.4 (C-1'), 40.8 (C-2'), 71.5 (C-3'), and 29.7 (C-4' and C-5') acyl group: δ 210.3 (C-1'), 46.4 (C-1), 27.4 (C-2), 12.4 (C-3), and 16.9 (C-4)[66]
Dauphinol C (**33**) $C_{26}H_{38}O_4$	*Garcinia dauphinensis* Madagascar[66]	^{1}H NMR[d] ($CDCl_3$) THB core: δ 5.79 (H-3) and 5.33 (OH) R_5 group: δ 2.65 (H-1), 2.53 (H-1), 2.82 (H-2), 5.18 (H-4), 2.55 (H-5), 2.39 (H-5), 4.81 (H-6), 1.52 (H-8), 1.70 (H-9), 1.62 (H-10), 1.59 (H-1'), 1.92 (H-2'), 4.67 (H-4'), and 1.70 (H-5') acyl group: δ 3.71 (H-1), 1.82 (H-2), 1.38 (H-2), 0.91 (H-3), and 1.16 (H-4) ^{13}C NMR[d] ($CDCl_3$) THB core: δ 104.7 (C-1), 159.3 (C-2), 95.2 (C-3), 160.2 (C-4), 106.9 (C-5), and 163.4 (C-6) R_5 group: δ 27.0 (C-1), 39.0 (C-2), 136.6 (C-3), 127.4 (C-4), 26.5 (C-5), 123.5 (C-6), 131.5 (C-7), 17.7 (C-8), 18.6 (C-9), 25.8 (C-10), 30.6 (C-1'), 35.9 (C-2'), 146.4 (C-3'), 109.8 (C-4'), and 22.6 (C-5') acyl group: δ 210.4 (C-1'), 46.2 (C-1), 27.1 (C-2), 12.1 (C-3), and 16.7 (C-4)[66]
Dauphinol D (hyperannulatin B) (**34**) $C_{26}H_{38}O_4$	*Garcinia dauphinensis* Madagascar[66] *Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR[d] ($CDCl_3$) THB core: δ 5.81 (H-3) and 5.28 (OH) R_5 group: δ 2.62 (H-1), 2.55 (H-1), 2.83 (H-2), 4.81 (H-4), 2.55 (H-5), 2.36 (H-5), 5.18 (H-6), 1.71 (H-8), 1.51 (H-9), 1.62 (H-10), 2.08 (H-1'), 2.17 (H-1'), 5.10 (H-2'), 1.63 (H-4'), and 1.71 (H-5') acyl group: δ 3.71 (H-1), 1.82 (H-2), 1.38 (H-2), 0.90 (H-3), and 1.15 (H-4) ^{13}C NMR[d] ($CDCl_3$) THB core: δ 106.9 (C-1), 159.7 (C-2), 95.4 (C-3), 160.1 (C-4), 104.8 (C-5), and 162.8 (C-6) R_5 group: δ 26.3 (C-1), 40.2 (C-2), 137.0 (C-3), 127.0 (C-4), 26.5 (C-5), 123.4 (C-6), 131.5 (C-7), 17.7 (C-8), 18.7 (C-9), 25.8 (C-10), 31.3 (C-1'), 123.2 (C-2'), 133.1 (C-3'), 18.1 (C-4'), and 25.9 (C-5') acyl group: δ 210.4 (C-1'), 46.2 (C-1), 27.1 (C-2), 12.1 (C-3), and 16.7 (C-4)[66]
Caespitate (**35**) $C_{17}H_{22}O_6$	*Helichrysum caespititium* South Africa[9] *Helichrysum niveum* South Africa[42]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.88 (H-3), 8.23 (OH-4), and 12.88 (OH-6) R_5 group: δ 3.42 (H-1), 5.38 (H-2), 4.73 (H-4), 2.05 (H-6), and 1.70 (H-7) acyl group: δ 3.89 (H-1), and 1.43 (H-2 and H-3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 104.0 (C-1), 159.4 (C-2), 95.3 (C-3), 160.7 (C-4), 105.8 (C-5), and 163.5 (C-6) R_5 group: δ 21.0 (C-1), 128.9 (C-2), 129.9 (C-3), 64.1 (C-4), 172.6 (C-5), 21.2 (C-6), and 21.1 (C-7) acyl group: δ 210.8 (C-1'), 39.2 (C-1), and 19.3 (C-2 and C-3)[42]
6-Demethylacronylin (**36**) $C_{13}H_{16}O_4$	*Acronychia laurifolia*[c 70]	NMR data not found
Caespitin (**37**) $C_{17}H_{24}O_4$	*Helichrysum caespititium* South Africa[71]	^{1}H NMR (80 MHz, $CDCl_3$/CD_3OD) δ 13.33, 5.90, 5.25, 3.22, 3.02, 2.65-2.03, 1.73, 1.65, 1.58, and 0.88 ^{13}C NMR[d] (DMSO-d_6) δ 163.4, 162.1, 159.8, 105.9, 103.6, 41.1, 33.7, 25.4, 22.3, 20.9, and 17.6 THB core: δ 103.6 (C-1 or C-3), 105.9 (C-1 or C-3), and 94.2 (C-5) prenyl group: δ 123.5 (C-2) and 129.3 (C-3) acyl group: δ 205.6 (C-1') and 27.5 (C-3)[71]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
(2,4,6-Trihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)prop-2-en-1-one[f] (**38**) $C_{20}H_{20}O_4$	*Helichrysum argyrolepis* South Africa[72]	NMR data not found
3'-(3,3-Dimethylallyl)-2',4',6'-trihydroxy-7,8-dihydrochalkon (**39**) $C_{20}H_{22}O_4$	*Helichrysum argyrolepis* South Africa[72]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.84 (H-5) prenyl group: δ 3.35 (H-1), 5.23 (H-2), 1.82 (H-4), and 1.77 (H-5) acyl group: δ 3.39 (H-1), 3.01 (H-2), and 7.25 (H-4 and H-8)[72]
1-(2',4'-Dihydroxy-6'-(3''-methyl-2''-butenyloxy)-5'-(3''-methyl-2''-butenyl)) phenylethanone (**40**) $C_{18}H_{24}O_4$	*Euodia lunu-ankenda* Sri Lanka[73]	NMR data not found
Olympicin A (**41**) $C_{21}H_{30}O_4$	*Hypericum olympicum* England[69]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 5.92 (H-3), 5.98 (H-5), 5.32 (OH-4), and 14.02 (OH-6) geranyl group:[a] δ 4.57 (H-1), 5.51 (H-2), 2.13 (H-4), 2.10 (H-5), 5.10 (H-6), 1.62 (H-8), 1.74 (s, H-9), and 1.69 (H-10) acyl group: δ 3.66 (H-1), 1.37 (H-2), 1.80 (H-2), 0.89 (H-3), and 1.12 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.0 (C-1), 162.6 (C-2), 91.5 (C-3), 161.9 (C-4), 96.5 (C-5), and 167.5 (C-6) geranyl group:[a] δ 65.7 (C-1), 118.2 (C-2), 142.3 (C-3), 39.5 (C-4), 26.3 (C-5), 123.6 (C-6), 132.0 (C-7), 17.7 (C-8), 16.7 (C-9), and 25.7 (C-10) acyl group: δ 210.4 (C-1'), 46.1 (C-1), 26.8 (C-2), 11.8 (C-3), and 16.6 (C-4)[69]
Melicopol (**42**) $C_{19}H_{26}O_6$	*Melicope broadbentiana* Australia[33]	^{1}H NMR (D_2O) THB core: δ 4.71 (H-3), 3.90 (OH-3), 6.01 (H-5), 7.15 (OH), and 13.25 (OH) geranyl group:[a] δ 4.53 (H-1), 5.50 (H-2 or H-6), 5.10 (H-2 or H-6), 2.12 (H-4 and H-5), 1.77 (H-8 and H-10), 1.67 (H-8 or H-10), and 1.62 (H-8 or H-10) acyl group: δ 3.90 (CH_3)[33]
1-[2',4'-Dihydroxy-6'-(3'',7''-dimethylocta-2'',6''-dienyloxy)-5'-(3''-methyl-2''-butenyl)]phenylethanone (**43**) $C_{23}H_{32}O_4$	*Euodia lunu-ankenda* Sri Lanka[73]	NMR data not found
3-Farnesyl-2,4,6-trihydroxyacetophenone (**44**) $C_{23}H_{32}O_4$	*Boronza ramose* Australia[48]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.88 (H-5) R_3 group: δ 3.37 (H-1), 5.26 (H-2), 1.94-2.16 (H-4, H-5, H-8, and H-9), 5.08 (H-6), 5.08 (H-10), 1.68 (H-12), 1.78 (H-13), 1.60 (H-14), and 1.60 (H-15) acyl group: δ 2.68 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 105.4 (C-1), 160.7 (C-2), 105.7 (C-3), 161.6 (C-4), 95.5 (C-5), and 162.6 (C-6) R_3 group: δ 21.7 (C-1), 121.6 (C-2), 140.2 (C-3), 39.9 (C-4 and C-8), 26.5 (C-5), 123.7 (C-6), 135.9 (C-7), 26.9 (C-9), 124.5 (C-10), 131.5 (C-11), 25.9 (C-12), 16.5 (C-13), 16.3 (C-14), and 17.9 (C-15) acyl group: δ 204.1 (C-1') and 33.0 (CH_3)[48]
Olympicin B (**45**) $C_{21}H_{30}O_5$	*Hypericum olympicum* England[69]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 5.90 (H-3), 5.99 (H-5), and 14.00 (OH-6) R_2 group: δ 4.58 (H-1), 5.30 (H-2), 2.81 (H-4), 5.68 (H-5), 5.66 (H-6), 1.35 (H-8 and H-10), and 1.74 (H-9) acyl group: δ 3.63 (H-1), 1.37 (H-2), 1.80 (H-2), 0.88 (H-3), and 1.12 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.9 (C-1), 162.4 (C-2), 91.7 (C-3), 162.1 (C-4), 96.6 (C-5), and 167.5 (C-6) R_2 group: δ 65.6 (C-1), 119.6 (C-2), 140.5 (C-3), 42.2 (C-4), 128.4 (C-5), 135.9 (C-6), 82.2 (C-7), 24.3 (C-8 and C-10), and 16.8 (C-9) acyl group: δ 210.3 (C-1'), 46.1 (C-1), 26.9 (C-2), 11.9 (C-3), and 16.7 (C-4)[69]
Hyperfaberol E (**46**) $C_{20}H_{28}O_5$	*Hypericum faberi* China[74]	^{1}H NMR (600 MHz, DMSO) THB core: δ 5.90 (H-5), 13.90 (OH-2), 10.26 (OH-4), and 10.78 (OH-6) R_3 group: δ 2.66 (H-1), 2.53 (H-1), 4.14 (H-2), 2.03 (H-4), 2.02 (H-5), 5.06 (H-6), 1.59 (H-8), 4.61 (H-9), 4.78 (H-9), and 1.52 (H-10) acyl group: δ 3.86 (H-1) and 1.02 (H-2 and H-3) ^{13}C NMR (150 MHz, DMSO) THB core: δ 102.8 (C-1), 164.1 (C-2), 104.2 (C-3), 163.0 (C-4), 94.5 (C-5), and 160.1 (C-6) R_3 group: δ 29.3 (C-1), 73.5 (C-2), 152.1 (C-3), 26.0 (C-4), 31.0 (C-5), 124.5 (C-6), 130.6 (C-7), 25.5 (C-8), 108.1 (C-9), and 17.5 (C-10) acyl group: δ 209.5 (C-1'), 38.1 (C-1), and 19.3 (C-2 and C-3)[74]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
Hyperfaberol C (**47**) $C_{21}H_{32}O_6$	*Hypericum faberi* China[74]	^{1}H NMR (600 MHz, DMSO) THB core: δ 5.97 (H-5), 14.14 (OH-2), 10.26 (OH-4), and 10.51 (OH-6) R_3 group: δ 3.06 (H-1), 5.11 (H-2), 1.82 (H-4), 2.10 (H-4), 1.12 (H-5), 1.52 (H-5), 3.14 (H-6), 1.01 (H-8), 1.66 (H-9), 0.94 (H-10), and 3.03 (H-11) acyl group: δ 3.89 (H-1) and 1.05 (H-2 and H-3) ^{13}C NMR (150 MHz, DMSO) THB core: δ 102.7 (C-1), 163.8 (C-2), 106.0 (C-3), 162.2 (C-4), 94.2 (C-5), and 159.6 (C-6) R_3 group: δ 20.9 (C-1), 122.7 (C-2), 133.8 (C-3), 36.4 (C-4), 29.2 (C-5), 74.4 (C-6), 76.8 (C-7), 21.6 (C-8), 16.1 (C-9), 19.6 (C-10), and 48.6 (C-11) acyl group: δ 209.5 (C-1'), 38.0 (C-1), and 19.3 (C-2 and C-3)[74]
Iso-hyperjovinol-A (**48**) $C_{20}H_{30}O_5$	*Hypericum jovis* Greece[62]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 5.85 (H-5) R_3 group: δ 3.35 (H-1), 5.24 (H-2), 2.05 (H-4), 1.49 (H-5), 1.43 (H-6), 1.20 (H-8 and H-10), and 1.80 (H-9) acyl group: δ 3.88 (H-1) and 1.16 (H-2 and H-3) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.0 (C-1), 162.8 (C-2), 105.8 (C-3), 160.9 (C-4 and C-6), and 95.2 (C -5) R_3 group: δ 21.4 (C-1), 122.1 (C-2), 138.8 (C-3), 39.2 (C-4), 22.3 (C-5), 43.1 (C-6), 71.6 (C-7), 29.1 (C-8 and C-10), and 16.1 (C-9) acyl group: δ 210.8 (C-1'), 39.8 (C-1), and 19.2 (C-2 and C-3)[62]
Hyperfaberol D (**49**) $C_{20}H_{28}O_5$	*Hypericum faberi* China[74]	^{1}H NMR (600 MHz, DMSO) THB core: δ 5.98 (H-5), 14.13 (OH-2), 10.26 (OH-4), and 10.52 (OH-6) R_3 group: δ 3.07 (H-1), 5.09 (H-2), 1.82 (H-4), 1.89 (H-4), 1.42 (H-5), 3.78 (H-6), 1.59 (H-8), 1.66 (H-9), 4.67 (H-10), and 4.79 (H-11) acyl group: δ 3.89 (H-1) and 1.05 (H-2 and H-3) ^{13}C NMR (150 MHz, DMSO) THB core: δ 102.6 (C-1), 163.8 (C-2), 105.9 (C-3), 162.2 (C-4), 94.2 (C-5), and 159.6 (C-6) R_3 group: δ 20.9 (C-1), 122.8 (C-2), 133.3 (C-3), 35.2 (C-4), 33.4 (C-5), 73.5 (C-6), 148.2 (C-7), 17.6 (C-8), 16.1 (C-9), and 109.8 (C-10) acyl group: δ 209.5 (C-1'), 38.0 (C-1), and 19.3 (C-2 and C-3)[74]
3'-Methyl-isohyperjovinol A (**50**) $C_{21}H_{32}O_5$	*Hypericum jovis* Greece[62]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 5.84 (H-5) R_3 group: δ 3.37 (H-1), 5.26 (H-2), 2.05 (H-4), 1.49 (H-5), 1.43 (H-6), 1.20 (H-8 and H-10), and 1.81 (H-9) acyl group: δ 3.73 (H-1), 1.84 (H-2), 1.40 (H-2), 0.91 (H-3), and 1.15 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.6 (C-1), 162.8 (C-2), 105.8 (C-3), 160.7 (C-4 and C-6), and 95.3 (C -5) R_3 group: δ 21.5 (C-1), 121.7 (C-2), 139.4 (C-3), 39.9 (C-4), 22.3 (C-5), 43.2 (C-6), 71.1 (C-7), 29.2 (C-8 and C-10), and 16.2 (C-9) acyl group: δ 210.3 (C-1'), 45.9 (C-1), 26.9 (C-2), 11.9 (C-3), and 16.7 (C-4)[62]
Crassipetalonol A (**51**) $C_{18}H_{24}O_5$	*Acronychia crassipetala* Australia[75]	^{1}H NMR (400 MHz, DMSO) THB core: δ 6.06 (H-5), 13.45 (OH-2), and 10.97 (OH-6) prenyl R_3 group: δ 3.11 (H-1), 5.07 (H-2), 1.59 (H-4), and 1.67 (H-5) prenyl R_4 group: δ 4.52 (H-1), 5.40 (H-2), 1.70 (H-4), and 1.75 (H-5) acyl group: δ 4.63 (CH_2) ^{13}C NMR (100 MHz, DMSO) THB core: δ 102.4 (C-1), 161.5 (C-2), 107.0 (C-3), 162.5 (C-4), 91.3 (C-5), and 160.7 (C-6) prenyl R_3 group: δ 20.9 (C-1), 122.9 (C-2), 129.9 (C-3), 25.4 (C-4), and 17.5 (C-5) prenyl R_4 group: δ 64.6 (C-1), 119.2 (C-2), 137.8 (C-3), 18.0 (C-4), and 25.5 (C-5) acyl group: δ 204.4 (C-1') and 68.2 (CH_2)[75]
Crassipetalone A (**52**) $C_{18}H_{24}O_4$	*Acronychia crassipetala* Australia[75]	NMR data not found
Acronyculatin S (**53**) $C_{14}H_{18}O_4$	*Mallotus oppositifolius* Cameroon[76]	^{1}H NMR (600 MHz, DMSO) THB core: δ 6.01 (H-5), 3.82 (OCH_3-4), and 13.93 (OH-6) prenyl group: δ 3.33 (H-1), 5.18 (H-2), 1.77 (H-4), and 1.83 (H-5) acyl group: δ 2.66 (CH_3) ^{13}C NMR (150 MHz, DMSO) THB core: δ 105.1 (C-1), 159.1 (C-2), 105.8 (C-3), 162.7 (C-4), 91.5 (C-5), and 165.6 (C-6) prenyl group: δ 21.2 (C-1), 121.3 (C-2), 135.5 (C-3), 25.6 (C-4), and 17.7 (C-5) acyl group: δ 203.3 (C-1') and 32.7 (CH_3)[76]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
2,6-Dihydroxy-4-geranyloxy-3-prenylacetophenone (**54**) $C_{23}H_{32}O_4$	*Evodia merrillii* Taiwan[46] *Melicope obtusifolia* Reunion Island[47]	^{1}H NMR[b] (300 MHz) THB core: δ 5.98 (H-5), 8.41 (OH-2 or OH-6), and 11.64 (OH-2 or OH-6) prenyl group: δ 3.31 (H-1), 5.17 (H-2), 1.79 (H-4), and 1.73 (H-5) geranyl group:[a] δ 4.51 (H-1), 5.42 (H-2), 2.09 (H-4 and H-5), 5.07 (H-6), 1.58 (H-8), 1.69 (H-9), and 1.66 (H-10) acyl group: δ 2.64 (CH_3) ^{13}C NMR[b] (75 MHz) THB core: δ 105.3 (C-1), 159.7 (C-2), 106.5 (C-3), 163.0 (C-4), 92.8 (C-5), and 162.5 (C-6) prenyl group: δ 21.6 (C-1), 121.9 (C-2), 134.9 (C-3), 25.8 (C-4), and 17.8 (C-5) geranyl group:[a]: δ 65.4 (C-1), 118.9 (C-2), 141.5 (C-3), 39.5 (C-4), 26.3 (C-5), 123.7 (C-6), 131.9 (C-7), 17.7 (C-8), 16.7 (C-9), and 25.6 (C-10) acyl group: δ 203.5 (C-1') and 32.8 (CH_3)[46]
Otogirin (**55**) $C_{21}H_{30}O_4$	*Hypericum erectum* South Korea[77] Japan[78,79] *Hypericum faberi* China[74]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 9.80 (OH-2), 5.96 (H-5), 9.60 (OH-6), and 2.03 (CH_3) geranyl group:[a] δ 4.55 (H-1), 5.46 (H-2), 2.10 (H-4 and H-5), 5.09 (H-6), 1.68 (H-8), and 1.72 (H-9 and H-10) acyl group: δ 3.90 (H-1) and 1.17 (H-2 and H-3) ^{13}C NMR (67.89 MHz, $CDCl_3$) THB core: δ 104.4 (C-1), 160.9 (C-2), 103.8 (C-3), 162.5 (C-4), 92.6 (C-5), 159.9 (C-6), and 7.3 (CH_3) geranyl group:[a] δ 65.4 (C-1), 119.0 (C-2), 141.4 (C-3), 39.5 (C-4), 26.3 (C-5), 123.7 (C-6), 131.9 (C-7), 25.6 (C-8), 16.7 (C-9), and 17.6 (C-10) acyl group: δ 210.5 (C-1'), 39.3 (C-1) and 19.3 (C-2 and C-3)[78]
4-Geranyloxy-3-prenyl-2,6,β-trihydroxyacetophenone (**56**) $C_{23}H_{32}O_5$	*Evodia merrillii* Taiwan[56] *Melicope obtusifolia* Reunion Island[47]	^{1}H NMR[d] ($CDCl_3$) δ 3.99 (OH), 8.80 (OH), and 11.03 (OH) THB core: δ 6.01 (H-5) prenyl group: δ 3.30 (H-1), 5.15 (H-2), 1.79 (H-4), and 1.73 (H-5) geranyl group:[a] δ 4.53 (H-1), 5.42 (H-2), 2.08 (H-4 and H-5), 5.07 (H-6), 1.59 (H-8), 1.70 (H-9), and 1.66 (H-10) acyl group: δ 4.78 (CH_2) ^{13}C NMR[d] ($CDCl_3$) THB core: δ 102.7 (C-1), 159.9 (C-2), 107.1 (C-3), 163.7 (C-4), 92.8 (C-5), and 162.8 (C-6) prenyl group: δ 21.5 (C-1), 121.7 (C-2), 135.0 (C-3), 17.8 (C-4), and 25.8 (C-5) geranyl group:[a] δ 65.6 (C-1), 118.7 (C-2), 141.8 (C-3), 39.4 (C-4), 26.3 (C-5), 123.7 (C-6), 131.9 (C-7), 17.7 (C-8), 16.7 (C-9), and 25.6 (C-10) acyl group: δ 201.8 (C-1') and 68.5 (CH_2)[56]
Hyperannulatin A (**57**) $C_{25}H_{36}O_4$	*Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 5.85 (H-5) R_3 group: δ 2.64 (H-1), 2.50 (H-1), 2.21 (H-2), 5.16 (H-4), 2.65 (H-5), 5.01 (H-6), 1.67 (H-8), 1.60 (H-9), 1.59 (H-10), 2.17 (H-1'), 2.11 (H-1'), 5.10 (H-2'), 1.69 (H-4'), and 1.60 (H-5') acyl group: δ 3.87 (H-1) and 1.17 (H-2 and H-3) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 104.2 (C-1), 162.4 (C-2), 106.9 (C-3), 160.5 (C-4), and 95.4 (C-5) R_3 group: δ 27.7 (C-1), 48.5 (C-2), 139.0 (C-3), 124.9 (C-4), 27.0 (C-5), 122.9 (C-6), 131.8 (C-7), 25.8 (C-8), 14.6 (C-9), 17.8 (C-10), 32.2 (C-1'), 123.2 (C-2'), 133.2 (C-3'), 25.9 (C-4'), and 18.2 (C-5') acyl group: δ 210.8 (C-1'), 39.3 (C-1), and 19.5 (C-2 and C-3)[35]
1-(3,5-Dihydroxy-1-((3-methylbut-2-enyl)oxy)phenyl)-2-methyl-1-methylbutan-1-one (**58**) $C_{17}H_{24}O_4$	*Hypericum calycinum* Switzerland[40]	^{1}H NMR (200 MHz, $CDCl_3$) THB core: δ 5.96 (H-3), 2.01 (H-5), 10.30, and 9.82 prenyl group: δ 4.5 (H-1), 5.44 (H-2), 1.79 (H-4 or H-5), and 1.71 (H-4 or H-5); acyl group: δ 2.97 (H-1), 2.26 (H-2), and 0.97 (H-3 and H-4) ^{13}C NMR (50 MHz, $CDCl_3$) THB core: δ 103.8 (C-1), 160.2 (C-2), 92.3 (C-3), 162.7 (C-4), 104.7 (C-5), 160.9 (C-6), and 7.2 (CH_3-5) prenyl group: δ 65.3 (C-1), 119.1 (C-2), 138.3 (C-3), 25.7 (C-4), and 18.2 (C-5); acyl group: δ 206.2 (C-1'), 52.9 (C-1), 25.4 (C-2), and 22.8 (C-3 and C-4)[40]
Adotogirin (**59**) $C_{22}H_{32}O_4$	*Hypericum erectum* Japan[79]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 5.96 (H-3) and 2.02 (CH_3-5) geranyl group:[a] δ 4.52 (H-1), 5.44 (H-2), 2.08 (H-4), 2.12 (H-5), 5.08 (H-6), 1.60 (H-8), 1.71 (H-9), and 1.67 (H-10) acyl group: δ 3.77 (H-1), 1.84 (H-2), 1.41 (H-2), 0.91 (H-3), and 1.16 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 104.3 (C-1), 160.8 (C-2), 92.5 (C-3), 162.5 (C-4), 103.9 (C-5), 160.2 (C-6), and 7.2 (CH_3-5) geranyl group:[a] δ 65.3 (C-1), 118.9 (C-2), 141.4 (C-3), 39.4 (C-4), 26.2 (C-5), 123.6 (C-6), 131.9 (C-7), 17.7 (C-8), 16.7 (C-9), and 25.6 (C-10) acyl group: δ 210.4 (C-1'), 45.9 (C-1), 27.0 (C-2), 11.9 (C-3), and 16.7 (C-4)[79]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
Empetrifelixin D (**60**) $C_{31}H_{46}O_4$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 6.20 (H-3), 12.12 (OH-2), and 7.61 (OH-6) geranyl group:[a] δ 3.34 (H-1), 5.16 (H-2), 2.08 (H-4), 2.11 (H-5), 5.06 (H-6), 1.67 (H-8), 1.81 (H-9), and 1.60 (H-10) R_4 group: δ 2.04 (H-2), 1.38 (H-3), 1.89 (H-3), 2.01 (H-4), 5.38 (H-6), 1.91 (H-7), 2.07 (H-7), 1.42 (H-8), 1.39 (H-9), and 1.65 (H-10) acyl group: δ 3.74 (H-1), 1.40 (H-2), 1.82 (H-2), 0.90 (H-3), and 1.14 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 109.8 (C-1), 162.5 (C-2), 99.5 (C-3), 160.1 (C-4), 105.3 (C-5), and 159.1 (C-6) geranyl group:[a] δ 22.4 (C-1), 121.9 (C-2), 139.2 (C-3), 39.6 (C-4), 26.3 (C-5), 123.6 (C-6), 131.9 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.6 (C-10) R_4 group: δ 84.8 (C-1), 44.1 (C-2), 24.2 (C-3), 30.9 (C-4), 134.0 (C-5), 120.4 (C-6), 26.6 (C-7), 24.1 (C-8), 24.2 (C-9), and 23.3 (C-10) acyl group: δ 210.4 (C-1'), 45.9 (C-1), 26.8 (C-2), 11.9 (C-3), and 16.7 (C-4)[3]
Empetrifelixin C (**61**) $C_{30}H_{44}O_4$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 6.21 (H-3), 12.14 (OH-2), and 7.57 (OH-6) geranyl group:[a] δ 3.34 (H-1), 5.16 (H-2), 2.07 (H-4), 2.11 (H-5), 5.05 (H-6), 1.67 (H-8), 1.81 (H-9), and 1.59 (H-10) R_4 group: δ 2.04 (H-2), 1.37 (H-3), 1.88 (H-3), 2.00 (H-4), 5.38 (H-6), 1.91 (H-7), 2.07 (H-7), 1.42 (H-8), 1.39 (H-9), and 1.65 (H-10) acyl group: δ 3.88 (H-1) and 1.16 (H-2 and H-3) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 109.8 (C-1), 162.6 (C-2), 99.5 (C-3), 160.1 (C-4), 104.8 (C-5), and 159.0 (C-6) geranyl group:[a] δ 22.4 (C-1), 121.9 (C-2), 139.3 (C-3), 39.6 (C-4), 26.3 (C-5), 123.6 (C-6), 131.9 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.6 (C-10) R_4 group: δ 84.8 (C-1), 44.1 (C-2), 24.2 (C-3), 30.9 (C-4), 134.0 (C-5), 120.4 (C-6), 26.6 (C-7), 24.1 (C-8), 24.3 (C-9), and 23.3 (C-10) acyl group: δ 210.6 (C-1'), 39.2 (C-1), and 19.2 (C-3 and C-4)[3]
Prereminol (**62**) $C_{14}H_{18}O_4$	*Remirea maritima*[c 49]	^{1}H NMR (100 MHz, C_5D_5N): δ 8.30, 8.10, 7.43, 6.40, 6.33, 4.35, 3.85, 0.2, and -4.7[49]
Empetrifelixin A (**63**) $C_{30}H_{44}O_4$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 6.06 (H-3), 6.04 (OH-4), and 13.91 (OH-6) geranyl group:[a] δ 3.38 (H-1), 5.28 (H-2), 2.07 (H-4), 2.10 (H-5), 5.05 (H-6), 1.67 (H-8), 1.80 (H-9), and 1.59 (H-10) R_2 group: δ 2.25 (H-2), 1.35 (H-3), 1.86 (H-3), 1.99 (H-4), 5.37 (H-6), 1.89 (H-7), 2.01 (H-7), 1.45 (H-8), 1.38 (H-9), and 1.65 (H-10) acyl group: δ 3.95 (H-1) and 1.17 (H-2 and H-3) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 107.7 (C-1), 157.6 (C-2), 98.0 (C-3), 160.6 (C-4), 106.3 (C-5), and 163.9 (C-6) geranyl group:[a] δ 21.6 (C-1), 121.7 (C-2), 139.5 (C-3), 39.6 (C-4), 26.3 (C-5), 123.6 (C-6), 132.0 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.7 (C-10) R_2 group: δ 86.1 (C-1), 42.6 (C-2), 24.5 (C-3), 30.9 (C-4), 134.1 (C-5), 120.2 (C-6), 26.8 (C-7), 23.9 (C-8), 24.3 (C-9), and 23.3 (C-10) acyl group: δ 211.4 (C-1'), 38.8 (C-1), 19.5 (C-2), and 19.6 (C-3)[3]
Empetrifelixin B (**64**) $C_{31}H_{46}O_4$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 6.06 (H-3 and OH-4), and 13.92 (OH-6) geranyl group:[a] δ 3.38 (H-1), 5.29 (H-2), 2.07 (H-4), 2.10 (H-5), 5.05 (H-6), 1.67 (H-8), 1.82 (H-9), and 1.59 (H-10) R_2 group: δ 2.25 (H-2), 1.35 (H-3), 1.86 (H-3), 1.98 (H-4), 5.37 (H-6), 1.88 (H-7), 2.01 (H-7), 1.44 (H-8), 1.38 (H-9), and 1.65 (H-10) acyl group: δ 3.87 (H-1), 1.42 (H-2), 1.75 (H-2), 0.85 (H-3), and 1.12 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 108.4 (C-1), 157.6 (C-2), 98.1 (C-3), 160.5 (C-4), 106.3 (C-5), and 163.7 (C-6) geranyl group:[a] δ 21.6 (C-1), 121.7 (C-2), 139.5 (C-3), 39.6 (C-4), 26.3 (C-5), 123.6 (C-6), 132.0 (C-7), 25.6 (C-8), 16.1 (C-9), and 17.7 (C-10) R_2 group: δ 86.1 (C-1), 42.5 (C-2), 24.4 (C-3), 30.8 (C-4), 134.0 (C-5), 120.2 (C-6), 26.8 (C-7), 24.0 (C-8), 24.4 (C-9), and 23.3 (C-10) acyl group: δ 211.3 (C-1'), 45.3 (C-1), 26.9 (C-2), 11.7 (C-3), and 17.0 (C-4)[3]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
Prenylacronylin (**65**) $C_{19}H_{26}O_4$	*Acronychia pedunculata* Sri Lanka[50,80,81] China[82] Thailand[83] Taiwan[51] Indonesia[84] *Euodia lunu-ankenda* Sri Lanka[73] *Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 3.70 (H-2), 6.26 (OH-4), and 13.58 (OH-6) prenyl R_3 group: δ 3.37 (H-1), 5.21 (H-2), 1.75 (H-4), and 1.81 (H-5) prenyl R_5 group: δ 3.34 (H-1), 5.21 (H-2), 1.74 (H-4), and 1.81 (H-5) acyl group: δ 2.68 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 108.98 (C-1), 159.16 (C-2), 112.65 (C-3), 160.67 (C-4), 110.98 (C-5), 161.61 (C-6), and 62.81 (OCH_3) prenyl R_3 group: δ 21.82 (C-1), 122.26 (C-2), 134.66 (C-3), 25.81 (C-4), and 17.90 (C-5) prenyl R_5 group: δ 22.77 (C-1), 121.67 (C-2), 134.51 (C-3), 25.85 (C-4), and 17.98 (C-5) acyl group: δ 203.60 (C-1') and 31.1 (CH_3)[80]
Laricifolin B (**66**) $C_{21}H_{30}O_4$	*Hypericum laricifolium* Peru[85]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.90 (H-3), 6.15 (OH-4), and 14.40 (OH-6) prenyl R_2 group: δ 4.51 (H-1), 5.48 (H-2), 1.76 (H-4), and 1.86 (H-5) prenyl R_5 group: δ 3.37 (H-1), 5.27 (H-2), 1.73 (H-4), and 1.80 (H-5) acyl group: δ 3.66 (H-1), 1.35 (H-2), 0.88 (H-3), and 1.11 (H-4) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 105.5 (C-1), 160.4 (C-2), 91.5 (C-3), 161.3 (C-4), 106.0 (C-5), and 164.7 (C-6) prenyl R_2 group: δ 65.3 (C-1), 118.6 (C-2), 138.5 (C-3), 18.1 (C-4), and 25.7 (C-5) prenyl R_5 group: δ 21.6 (C-1), 121.9 (C-2), 135.6 (C-3), 17.9 (C-4), and 25.8 (C-5) acyl group: δ 210.5 (C-1'), 46.1 (C-1), 26.9 (C-2), 11.8 (C-3), and 16.5 (C-4)[85]
Laricifolin A (**67**) $C_{20}H_{28}O_4$	*Hypericum laricifolium* Peru[85]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 5.90 (H-3), 6.15 (OH-4), and 14.45 (OH-6) prenyl R_2 group: δ 4.51 (H-1), 5.48 (H-2), 1.76 (H-4), and 1.86 (H-5) prenyl R_5 group: δ 3.37 (H-1), 5.27 (H-2), 1.73 (H-4), and 1.80 (H-5) acyl group: δ 3.80 (H-1) and 1.14 (H-2 and H-3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 105.5 (C-1), 160.5 (C-2), 91.5 (C-3), 161.3 (C-4), 106.0 (C-5), and 164.7 (C-6) prenyl R_2 group: δ 65.4 (C-1), 118.7 (C-2), 138.7 (C-3), 18.2 (C-4), and 25.7 (C-5) prenyl R_5 group: δ 21.6 (C-1), 121.9 (C-2), 135.6 (C-3), 17.9 (C-4), and 25.8 (C-5) acyl group: δ 210.6 (C-1'), 39.4 (C-1), and 19.4 (C-2 and C-3)[85]
2,4,6-Trihydroxy-1-(2'-methyl-butanoyl)-3-(2'',3''-epoxy-3''-methyl-butyl)-5-(3'''-methyl-2'''-butenyl)-benzene (**68**) $C_{21}H_{30}O_5$	*Hypericum foliosum* England[86]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 14.25 (H-2 or H-6) and 14.26 (H-2 or H-6) prenyl group: δ 3.40 (H-1), 5.28 (H-2), 1.79 (H-4), and 1.84 (H-5) R_3 group: δ 2.61 (H-1), 2.86 (H-1), 3.81 (H-2), 1.39 (H-4), and 1.42 (H-5) acyl group: δ 3.74 (H-1), 1.43 (H-2), 1.85 (H-2), 0.91 (H-3), and 1.17 (H-4) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 105.6 (C-1), 153.9 (C-2 or C-6), 163.0 (C-2 or C-6), 160.0 (C-4), 105.7 (C-3 or C-5), and 97.8 (C-3 or C-5) prenyl group: δ 21.9 (C-1), 122.1 (C-2), 136.5 (C-3), 26.1 (C-4), and 18.1 (C-5) R_3 group: δ 26.2 (C-1), 68.9 (C-2), 78.3 (C-3), 24.9 (C-4), and 22.1 (C-5) acyl group: δ 210.7 (C-1'), 46.4 (C-1), 27.1 (C-2), 12.1 (C-3), and 17.0 (C-4)[86]
4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3''-methyl-but-2''-enyl)-5-(3'''-methyl-2'''-butanoyl)-benzene (**69**) $C_{19}H_{26}O_5$	*Acronychia oligophlebia* China[87]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 3.73 (OCH_3-2), 8.64 (OH-4), and 13.74 (OH-6) prenyl group: δ 3.34 (H-1), 5.22 (H-2), 1.79 (H-4), and 1.72 (H-5) R_5 group: δ 3.82 (H-1), 2.84 (H-3), and 1.17 (H-4 and H-5) acyl group: δ 2.68 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 109.2 (C-1), 160.6 (C-2), 114.8 (C-3), 162.4 (C-4), 105.5 (C-5), 161.5 (C-6), and 62.9 (OCH_3) prenyl group: δ 23.1 (C-1), 122.8 (C-2), 133.4 (C-3), 18.1 (C-4), and 25.9 (C-5) R_5 group: δ 34.7 (C-1), 217.8 (C-2), 41.7 (C-3), and 17.9 (C-4 and C-5) acyl group: δ 203.8 (C-1') and 31.1 (CH_3)[87]
Acronyculatin R (**70**) $C_{19}H_{26}O_5$	*Acronychia oligophlebia* China[88]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 3.72 (OCH_3-2), 13.69 (OH-6), and 8.91 (OH-4) R_5 group: δ 2.75 (H-1), 3.15 (H-1), 4.33 (H-2), 5.01 (H-4), 4.87 (H-4), and 1.85 (H-5) prenyl group: δ 3.33 (H-1), 5.21 (H-2), 1.70 (H-4), and 1.78 (H-5) acyl group: δ 2.69 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 108.9 (C-1), 160.1 (C-2), 115.0 (C-3), 162.4 (C-4), 109.5 (C-5), 162.1 (C-6), and 62.8 (OCH_3-2) R_5 group: δ 29.0 (C-1), 77.8 (C-2), 147.2 (C-3), 110.5 (C-4), and 18.6 (C-5) prenyl group: δ 23.1 (C-1), 123.3 (C-2), 132.2 (C-3), 25.9 (C-4), and 18.1 (C-5) acyl group: δ 203.7 (C-1') and 31.2 (CH_3)[88]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3”-methyl-but-2”-enyl)-5-(3’’-methyl-but-1”-enyl)-benzene (**71**) $C_{19}H_{26}O_4$	*Acronychia oligophlebia* China[87]	^{1}H NMR (300 MHz, CD_3OD) THB core: δ 3.73 (OCH_3-2) prenyl group: δ 3.34 (H-1), 5.21 (H-2), 1.80 (H-4), and 1.71 (H-5) R_3 group: δ 6.36 (H-1), 6.35 (H-2), 2.47 (H-3), and 1.12 (H-4 and H-5) acyl group: δ 2.69 (CH_3) ^{13}C NMR (75 MHz, CD_3OD) THB core: δ 109.6 (C-1), 161.1 (C-2), 111.1 (C-3), 162.8 (C-4), 115.7 (C-5), 161.3 (C-6), and 63.4 (OCH_3-2) prenyl group: δ 23.6 (C-1), 124.4 (C-2), 132.5 (C-3), 18.0 (C-4), and 25.9 (C-5) R_3 group: δ 117.8 (C-1), 143.8 (C-2), 33.9 (C-3), and 23.0 (C-4 and C-5) acyl group: δ 205.7 (C-1’) and 31.3 (CH_3)[87]
Acronyculatin F (**72**) $C_{19}H_{28}O_4$	*Acronychia pedunculata* Thailand[83]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 3.70 (OCH_3-2), 5.95 (OH-4), and 13.47 (OH-6) prenyl group: δ 3.38 (H-1), 5.22 (H-2), 1.79 (H-4), and 1.85 (H-5) R_5 group: δ 2.57 (H-1), 2.60 (H-1), 1.37 (H-2), 1.38 (H-2), 1.61 (H-3), and 0.95 (H-4 and H-5) acyl group: δ 2.68 (CH_3) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 109.0 (C-1), 158.7 (C-2), 111.5 (C-3), 160.1 (C-4), 113.6 (C-5), and 162.1 (C-6) prenyl group: δ 22.9 (C-1), 121.8 (C-2), 136.3 (C-3), 25.9 (C-4), and 18.0 (C-5) R_5 group: δ 20.7 (C-1), 37.9 (C-2), 28.4 (C-3), and 22.6 (C-4 and C-5) acyl group: δ 203.6 (C-1’) and 31.2 (CH_3)[83]
1-(4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3’’-hydroxy-3’’-methyl-but-1”-enoyl)-5-(3”- methyl-but-2”-enyl))benzene (**73**) $C_{19}H_{26}O_5$	*Acronychia oligophlebia* China[87]	^{1}H NMR (300 MHz, $CDCl_3$) THB core: δ 3.76 (OCH_3-2) and 13.74 (OH-6) prenyl group: δ 3.28 (H-1), 5.22 (H-2), 1.79 (H-4), and 1.67 (H-5) R_3 group: δ 5.60 (H-1), 6.50 (H-2), and 1.44 (H-4 and H-5) acyl group: δ 2.68 (CH_3) ^{13}C NMR (75 MHz, $CDCl_3$) THB core: δ 108.8 (C-1), 157.0 (C-2), 107.0 (C-3), 163.6 (C-4), 113.3 (C-5), 158.1 (C-6), and 63.2 (OCH_3-2) prenyl group: δ 21.6 (C-1), 122.3 (C-2), 131.5 (C-3), 18.0 (C-4), and 26.0 (C-5) R_3 group: δ 128.1 (C-1), 116.9 (C-2), 77.4 (C-3), and 28.3 (C-4 and C-5) acyl group: δ 203.3 (C-1’) and 31.4 (CH_3)[87]
Empetrikajaforin (**74**) $C_{31}H_{46}O_4$	*Hypericum empetrifolium* Greece[3]	^{1}H NMR (600 MHz, $CDCl_3$) THB core: δ 5.75 (H-3), 6.11 (OH-4), and 14.57 (OH-6) geranyl group:[a] δ 3.38 (H-1), 5.28 (H-2), 2.08 (H-4), 2.10 (H-5), 5.05 (H-6), 1.67 (H-8), 1.81 (H-9), and 1.59 (H-10) R_2 group: δ 4.38 (H-1), 1.12 (H-2), 2.45 (H-2), 1.77 (H-3), 1.25 (H-4), 1.80 (H-4), 1.42 (H-5), 2.10 (H-5), 0.96 (H-8 and H-10), and 0.92 (H-9) acyl group: δ 3.96 (H-1), 1.46 (H-2), 1.80 (H-2), 0.87 (H-3), and 1.17 (H-4) ^{13}C NMR (150 MHz, $CDCl_3$) THB core: δ 105.5 (C-1), 160.7 (C-2), 92.9 (C-3), 161.5 (C-4), 105.7 (C-5), and 164.9 (C-6) geranyl group:[a] δ 21.5 (C-1), 121.7 (C-2), 139.6 (C-3), 39.7 (C-4), 26.3 (C-5), 123.6 (C-6), 132.0 (C-7), 25.6 (C-8), 16.2 (C-9), and 17.7 (C-10) R_2 group: δ 85.5 (C-1), 37.3 (C-2), 44.7 (C-3), 27.9 (C-4), 27.3 (C-5), 49.5 (C-6), 47.7 (C-7), 19.0 (C-8), 19.7 (C-9), and 14.0 (C-10) acyl group: δ 210.6 (C-1’), 45.5 (C-1), 26.4 (C-2), 11.7 (C-3), and 17.8 (C-4)[3]
Acronyculatin Q (**75**) $C_{20}H_{30}O_5$	*Acronychia oligophlebia* China[88]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 3.73 (OCH_3-2), 13.59 (OH-6), and 9.54 (OH-4) R_5 group: δ 4.92 (H-1), 1.81 (H-2), 1.43 (H-2), 1.83 (H-3), 0.95 (H-4), 0.96 (H-5), and 3.39 (H-6) prenyl group: δ 3.28 (H-1), 5.21 (H-2), 1.70 (H-4), and 1.77 (H-5) acyl group: δ 2.68 (CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 108.5 (C-1), 160.8 (C-2), 108.9 (C-3), 162.2 (C-4), 114.9 (C-5), 161.3 (C-6), and 62.8 (OCH_3-2) R_5 group: δ 78.2 (C-1), 44.3 (C-2), 24.9 (C-3), 21.9 (C-4), 23.5 (C-5), and 57.8 (C-6) prenyl group: δ 22.5 (C-1), 123.4 (C-2), 131.6 (C-3), 25.8 (C-4), and 18.0 (C-5) acyl group: δ 203.7 (C-1’) and 31.1 (CH_3)[88]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^1H and ^{13}C NMR (chemical shift, δ / ppm)
4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3”-methyl-but-2”-enyl)-5-(3’”-hydroxy-3’”-methyl-but-1’”-enyl)-benzene (**76**) $C_{19}H_{26}O_5$	*Acronychia oligophlebia* China[87]	^1H NMR (400 MHz, $CDCl_3$) THB core: δ 3.72 (OCH_3-2) and 13.51 (OH-6) prenyl group: δ 3.24 (H-1), 5.15 (H-2), 1.78 (H-4), and 1.69 (H-5) R_5 group: δ 5.50 (H-1), 6.67 (H-2), and 1.43 (H-4 and H-5) acyl group: δ 2.67 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 109.1 (C-1), 161.1 (C-2), 115.0 (C-3), 158.7 (C-4), 106.1 (C-5), 159.1 (C-6), and 62.9 (OCH_3) prenyl group: δ 22.5 (C-1), 123.3 (C-2), 131.3 (C-3), 18.1 (C-4), and 25.9 (C-5) R_5 group: δ 126.8 (C-1), 116.3 (C-2), 78.0 (C-3), and 28.5 (C-4 and C-5) acyl group: δ 203.6 (C-1’) and 31.1 (CH_3)[87]
4,6-Dihydroxy-1-ethanoyl-2-methoxy-3-(3”-methyl-but-2”-enyl)-5-(3’”-methyl-but-1’”-enyl)-benzene (**77**) $C_{19}H_{26}O_4$	*Acronychia oligophlebia* China[87]	^1H NMR (300 MHz, CD_3OD) THB core: δ 3.72 (OCH_3-2) prenyl group: δ 3.30 (H-1), 5.19 (H-2), 1.76 (H-4), and 1.66 (H-5) R_5 group: δ 5.87 (H-1), 5.69 (H-2), 2.21 (H-3), and 0.92 (H-4 and H-5) acyl group: δ 2.66 (CH_3) ^{13}C NMR (75 MHz, CD_3OD) THB core: δ 109.3 (C-1), 161.7 (C-2), 115.5 (C-3), 161.3 (C-4), 109.9 (C-5), 162.1 (C-6), and 63.4 (OCH_3-2) prenyl group: δ 23.7 (C-1), 124.6 (C-2), 132.0 (C-3), 18.0 (C-4), and 25.9 (C-5) R_5 group: δ 117.1 (C-1), 146.2 (C-2), 30.0 (C-3), and 22.7 (C-4 and C-5) acyl group: δ 204.9 (C-1’) and 31.2 (CH_3)[87]
Hyperjaponol J (**78**) $C_{23}H_{34}O_4$	*Hypericum japonicum* China[68]	^1H NMR (400 MHz, $CDCl_3$) THB core: δ 2.13 (CH_3-3 and CH_3-5) geranyl group:[a] δ 4.32 (H-1), 5.56 (H-2), 2.09 (H-4), 2.11 (H-5), 5.11 (H-6), 1.69 (H-8 and H-9), and 1.61 (H-10) acyl group: δ 3.79 (H-1), 1.41 (H-2), 1.84 (H-2), 0.92 (H-3), and 1.17 (H-4) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 107.0 (C-1), 158.2 (C-2 and C-6), 109.1 (C-3 and C-5), 161.7 (C-4), and 8.8 (CH_3-3 and CH_3-5) geranyl group:[a] δ 70.0 (C-1), 119.6 (C-2), 141.9 (C-3), 39.8 (C-4), 26.5 (C-5), 123.9 (C-6), 132.0 (C-7), 25.8 (C-8), 16.6 (C-9), and 17.8 (C-10) acyl group: δ 211.5 (C-1’), 46.5 (C-1), 27.1 (C-2), 12.1 (C-3), and 16.8 (C-4)[68]
Hyperjaponol K (**79**) $C_{22}H_{32}O_4$	*Hypericum japonicum* China[68]	^1H NMR (400 MHz, $CDCl_3$) THB core: δ 2.13 (CH_3-3 and CH_3-5) geranyl group:[a] δ 4.32 (H-1), 5.55 (H-2), 2.09 (H-4), 2.11 (H-5), 5.10 (H-6), 1.69 (H-8 and H-9), and 1.61 (H-10) acyl group: δ 3.94 (H-1) and 1.19 (H-2 and H-3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 106.5 (C-1), 158.2 (C-2 and C-6), 109.1 (C-3 and C-5), 161.8 (C-4), and 8.8 (CH_3-3 and CH_3-5) geranyl group:[a] δ 70.0 (C-1), 119.6 (C-2), 142.0 (C-3), 39.8 (C-4), 26.5 (C-5), 123.9 (C-6), 132.0 (C-7), 25.8 (C-8), 16.6 (C-9), and 17.8 (C-10) acyl group: δ 211.7 (C-1’), 39.8 (C-1), and 19.4 (C-2 and C-3)[68]
2-Acetyl-3,5-dihydroxy-1-geranoxy-6-methyl-4-(2-methyl)-butyryl-benzene (**80**) $C_{24}H_{34}O_5$	*Hypericum japonicum* China[89]	^1H NMR (300 MHz, $CDCl_3$) THB core: δ 2.12 (H-5) and 9.45 (OH-2 and OH-4) geranyl group:[a] δ 4.32 (H-1), 5.55 (H-2), 2.10 (H-4), 2.12 (H-5), 5.10 (H-6), 1.68 (H-8), 1.68 (H-9), and 1.61 (H-10) acyl R_1 group: δ 2.16 (CH_3) acyl R_3 group: δ 3.78 (H-2), 1.85 (H-3), 1.41 (H-3), 0.91 (H-4), and 1.18 (H-5) ^{13}C NMR (75 MHz, $CDCl_3$) THB core: δ 106.8 (C-1), 157.9 (C-2), 108.8 (C-3), 157.9 (C-4), 108.8 (C-5), and 61.5 (C-6) geranyl group:[a] δ 69.7 (C-1), 119.4 (C-2), 141.6 (C-3), 39.5 (C-4), 26.2 (C-5), 123.7 (C-6), 131.8 (C-7), 25.6 (C-8), 16.4 (C-9), and 17.6 (C-10) acyl R_1 group: δ 205.6 (C-1’) and 30.8 (CH_3) acyl R_3 group: δ 211.2 (C-1), 46.3 (C-2), 26.8 (C-3), 11.9 (C-4), and 16.6 (C-5)[89]
Acronyculatin A (**81**) $C_{15}H_{18}O_5$	*Acronychia pedunculata* Taiwan[90] *Acronychia pubescens* Australia[54]	^1H NMR (300 MHz, $CDCl_3$) THB core: δ 14.63 (OH-2), 3.86 (H-6), and 13.13 (OH-4) prenyl group: δ 3.27 (H-1), 5.17 (H-2), 1.77 (H-4), and 1.70 (H-5) acyl R_1 group: δ 2.68 (CH_3) acyl R_3 group: δ 10.30 (COH) ^{13}C NMR (75 MHz, $CDCl_3$) THB core: δ 106.9 (C-1), 168.8 (C-2), 107.1 (C-3), 168.9 (C-4), 114.9 (C-5), 168.5 (C-6), and 62.7 (OCH_3) prenyl group: δ 21.9 (C-1), 121.8 (C-2), 132.6 (C-3), 25.7 (C-4), and 17.9 (C-5) acyl R_1 group: δ 213.1 (C-1’) and 31.0 (CH_3) acyl R_3 group: δ 193.4 (COH)[90]

Table 2. Prenylated-geranylated monocyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR (chemical shift, δ / ppm)
1-Acetyl-4-isopentenyl-6-methylphloroglucinol (**82**) $C_{14}H_{18}O_4$	*Leucanthemopsis pulverulenta* Spain[91]	^{1}H NMR (60 MHz, $CDCl_3$) THB core: δ 5.82 (H-3), 5.68 (H-5), 13.75 (OH-6), and 3.75 (OCH_3) prenyl group: δ 4.40 (H-1), 5.34 (H-2), 1.72 (H-4), and 1.78 (H-5) acyl group: δ 2.48 (CH_3)[91]
1-Acetyl-3-hydroxy-2,6-dimethyl-4-isopentenylphloroglucinol (**83**) $C_{15}H_{20}O_4$	*Leucanthemopsis pulverulenta* Spain[91]	^{1}H NMR (60 MHz, $CDCl_3$) THB core: δ 6.06 (H-3), 3.69 (OCH_3), 3.90 (OCH_3), and 7.95 (OH-5) prenyl group: δ 4.45 (H-1), 5.35 (H-2), and 1.73 (H-4 and H-5) acyl group: δ 2.57 (CH_3)[91]
Melibarbinon B (**84**) $C_{15}H_{20}O_4$	*Melicope barbigera* United States[92]	^{1}H NMR (600 MHz, DMSO) THB core: δ 6.21 (H-5), 13.98 (OH-2), 3.87 (OCH_3-4), and 3.92 (OCH_3-6) prenyl group: δ 2.62 (H-1), 2.71 (H-1), 4.14 (H-2), 4.51 (H-4), 4.54 (H-4), and 1.69 (H-5) acyl group: δ 2.56 (CH_3) ^{13}C NMR (150 MHz, DMSO) THB core: δ 105.0 (C-1), 163.1 (C-2), 106.0 (C-3), 164.1 (C-4), 87.1 (C-5), and 161.8 (C-6) prenyl group: δ 28.6 (C-1), 73.5 (C-2), 148.1 (C-3), 109.7 (C-4), and 16.9 (C-5) acyl group: δ 203.0 (C-1') and 32.9 (CH_3)[92]
2,4-Dihydroxy-3,6-dimethoxy-5-(3',3'-dimethylallyl)-butyrophenone (**85**) $C_{17}H_{24}O_4$	*Leontonyx spathulatus* South Africa[41]	^{1}H NMR (270 MHz, $CDCl_3$) THB core: δ 12.83 (OH-2 and OH-4), 3.89 (H-3 or H-6), and 3.90 (H-3 or H-6) prenyl group: δ 3.30 (H-1), 5.20 (H-2), 1.67 (H-4), and 1.73 (H-5) acyl group: δ 3.05 (H-1), 1.50 (H-2), and 0.98 (H-3)[41]
Acronyculatin P (**86**) $C_{20}H_{28}O_4$	*Acronychia pedunculata* Indonesia[84]	^{1}H NMR (400 MHz, $CDCl_3$) THB core: δ 13.43 (OH-6) and 3.71 (OCH_3-2 and OCH_3-4) R_5 group: δ 6.40 (H-1), 6.55 (H-2), 2.48 (H-3), and 1.10 (H-4 and H-5) prenyl group: δ 3.29 (H-1), 5.16 (H-2), 1.78 (H-4), and 1.69 (H-5) acyl group: δ 2.71 (CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) THB core: δ 111.9 (C-1), 159.6 (C-2), 120.4 (C-3), 163.5 (C-4), 116.4 (C-5), 161.5 (C-6), 60.4 (OCH_3-4), and 63.0 (OCH_3-2) R_5 group: δ 116.7 (C-1), 143.1 (C-2), 32.9 (C-3), and 22.6 (C-4 and C-5) prenyl group: δ 23.2 (C-1), 123.8 (C-2), 131.6 (C-3), 17.9 (C-4), and 25.8 (C-5) acyl group: δ 204.7 (C-1') and 31.4 (CH_3)[84]
1'-(2,4-Dihydroxy-3-(3''-methylbut-2''-enyl)-5-(1'''-ethoxy-3'''-methylbutyl)-6'-methoxy)-phenylethanone (**87**) $C_{21}H_{32}O_5$	*Acronychia pedunculata* China[82]	^{1}H NMR (500 MHz, $CDCl_3$) THB core: δ 13.60 (OH-2 or OH-4), 9.84 (OH-2 or OH-4), and 3.72 (H-6) prenyl group: δ 3.27 (H-1), 5.20 (H-2), 1.70 (H-4), and 1.77 (H-5) R_5 group: δ 5.00 (H-1), 3.52 (H-2), 3.61 (H-2), 1.23 (H-3), 1.40 (H-4), 1.80 (H-4), 1.84 (H-5), 0.95 (H-6), and 0.96 (H-7) acyl group: δ 2.67 (CH_3) ^{13}C NMR (125 MHz, $CDCl_3$) THB core: δ 108.2 (C-1), 160.9 (C-2), 114.7 (C-3), 162.3 (C-4), 109.4 (C-5), and 160.5 (C-6) prenyl group: δ 22.4 (C-1), 123.2 (C-2), 131.5 (C-3), 25.7 (C-4), and 17.9 (C-5) R_5 group: δ 75.7 (C-1), 65.7 (C-2), 15.1 (C-3), 44.1 (C-4), 24.7 (C-5), 23.4 (C-6), and 21.7 (C-7) acyl group: δ 203.5 (C-1') and 31.0 (CH_3)[82]
Acronyculatin C (**88**) $C_{19}H_{26}O_5$	*Acronychia pedunculata* Taiwan[90]	^{1}H NMR (300 MHz, $CDCl_3$) THB core: δ 15.56 (OH-2), 3.77 (H-6), and 15.12 (OH-4) prenyl group: δ 3.28 (H-1), 5.18 (H-2), 1.77 (H-4), and 1.69 (H-5) acyl R_1 group: δ 2.69 (CH_3) acyl R_3 group: δ 3.03 (H-2), 2.27 (H-3), 0.98 (H-4), and 0.97 (H-5) ^{13}C NMR (75 MHz, $CDCl_3$) THB core: δ 107.3 (C-1), 174.1 (C-2), 107.4 (C-3), 171.0 (C-4), 115.3 (C-5), 168.6 (C-6), and 62.6 (OCH_3) prenyl group: δ 22.3 (C-1), 122.3 (C-2), 132.2 (C-3), 25.7 (C-4), and 17.9 (C-5) acyl R_1 group: δ 203.8 (C-1') and 31.0 (CH_3) acyl R_3 group: δ 207.0 (C-1), 53.3 (C-2), 24.9 (C-3), and 22.8 (C-4 and C-5)[90]

[a]*trans* geranyl; [b]solvent use in NMR analysis was not found in the reference; [c]geographic location not found; [d]magnetic field strength was not found in the reference; [e]*cis* geranyl; [f]IUPAC name. NMR: nuclear magnetic resonance; THB: 1,3,5-trihydroxybenzene.

structure, associated with high reactivity and significant instability, which can induce oxidative stress in bacteria. Compound **28** was isolated from *H. jovis* in cyclohexane and cited as having significant anti-inflammatory activity, with half maximal inhibitory concentration (IC_{50}) values of 34.4.[45,62,69] Further, **29** was isolated from the aerial parts, in petroleum ether, of *H. empetrifolium*, showing antiproliferative activity in microvascular and endothelial cells.[3]

The genus *Garcinia* is studied because it has several chemical constituents of pharmacological interest, including phloroglucinols. Derivatives **31**-**34** were related to *G. dauphinensis*, being isolated from ethanolic extracts of the plant's roots and their structures elucidated by spectroscopic data. Compound **34** exhibited promising growth inhibitory activity against A2870 ovarian cancer cells, (IC_{50} = 4.5 ± 0.9 µM) and also showed antiplasmodial activity against the drug-resistant Dd2 strain of *Plasmodium falciparum* (IC_{50} = 0.8 ± 0.1 µM). Derivatives **31**-**32** were isolated from the ethanolic extract of *G. dauphinensis* roots, but do not show potential biological activity.[66]

The phloroglucinols **36**-**50** have the THB ring functionalized by aliphatic acyl groups at C-1, hydroxyl or *O*-prenyl or *O*-geranyl at C-2, prenyl or geranyl substituents at C-3, and two hydroxyl groups at C-4 and C-5 (Figures 5 and 8; Tables 1-2).

The prenylated compound **36** was associated with the species *Acronychia laurifolia*, and no mention of extraction and isolation methods was provided in the report.[70] Metabolite **37** was obtained from the ethyl acetate extract of *Helichrysum caespititium* and showed antimicrobial activity, with significant inhibition of *Staphylococcus aureus*, *Streptococcus pyogenes*, *Cryptococcus neoformans*, *Trichophyton rubrum*, *T. mentagrophytes* and *Microsporum canis*.[71]

Prenylated derivatives **38** and **39** were isolated from aerial parts of *H. argyrolepis* (ether/petroleum ether, 1:1).[72] Obtained from *Euodia lunu-ankenda* (CH_2Cl_2/CH_3OH), compounds **40** and **43** showed antifungal activity.[73] The genus *Melicope* has a variety of interesting classes of biosynthesized compounds. In this study, compound **42** stand out with a geranylated structure and with a methoxy substituent linked to the acyl group, which was isolated from the extract of the bark of *M. broadbentiana*, in ether/petroleum ether/CH_3OH.[32] Compound **44** was associated with the aerial parts of *B. ramose* (extract: petroleum ether, ethyl acetate and CH_3OH), without mention of biological activities.[48]

Derivatives **45**-**50** were isolated from species of the genus *Hypericum* and proved to be biologically relevant: **45** from *H. olympicum* (aerial parts in hexane/CH_2Cl_2/CH_3OH) and exhibited minimum inhibitory concentrations (MICs) of 0.51 mg L^{-1} against multidrug-resistant *Staphylococcus aureus* strains.[69] Compounds **46**, **47** and **49** from *H. faberi* (methanolic extract of whole plants) exhibited cytotoxicity against the human esophageal cancer cell line (ECA-109) and against the pancreatic tumor cell line (PANC-1) *in vitro*.[74] Compounds **48** and **50** were isolated from extracts in cyclohexane of aerial parts of *H. jovis*.[62]

Considering compounds **51**-**57** (Figures 5 and 9; Tables 1-2), the prenylated derivatives **51**-**52**, sequentially extracted in hexane/dichloromethane/CH_3OH/water from *A. crassipetal* fruits showed activity against *S. aureus* (moderate in **51** and greater than the antibiotic chloramphenicol in **52**).[75] Derivative **53** was isolated from *M. oppositifolius* leaf extracts using a mixture of CH_2Cl_2/CH_3OH (1:1), and showed inhibitory activity against bacterial strains *E. coli*, *S. aureus*, *S. typhi* and *P. aeruginosa* with MIC ranging from 3.125 to 50 µg mL^{-1}.[76] Compounds **54** and **56** were identified in the species *E. merrillii* from the fruit extract in 95% CH_3CH_2OH.[46,56] From *H. erectum*, compound **55** was isolated and found to be a potent antibacterial agent against *S. aureus* and

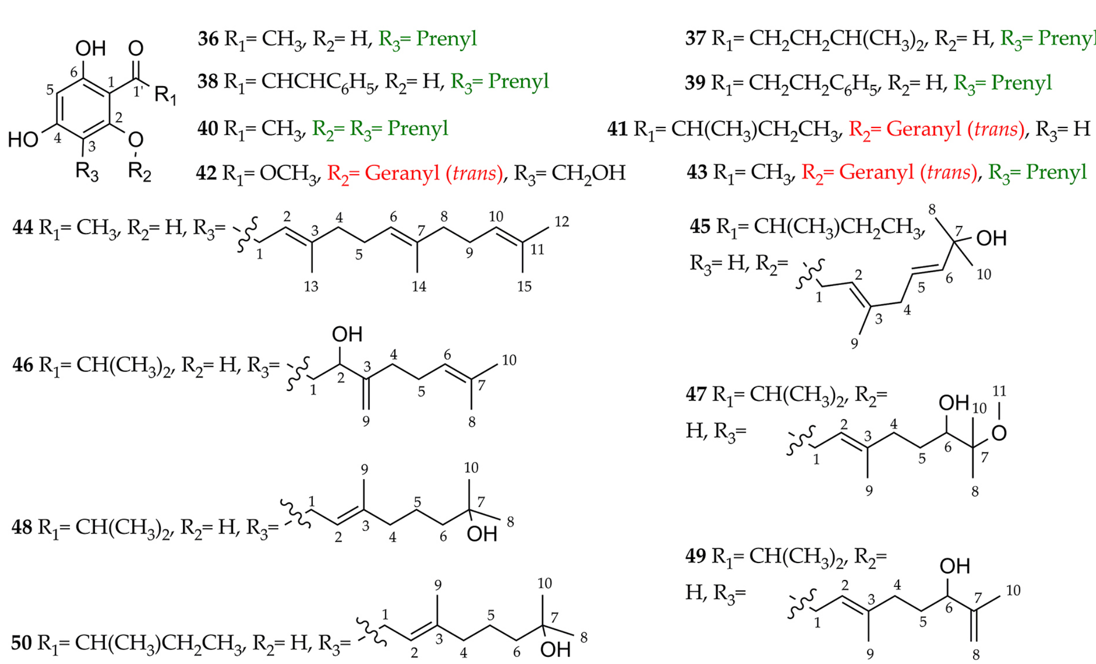


Figure 8. Monocyclic monomeric derivatives of acylphloroglucinols **36**-**50**.

B. subtilis.[77-79] Obtained from the hexane extract of the aerial parts of *H. anulatum*, derivative **57** was tested against tumor cells (HL-60, HL-60/DOX, MDA-MB, SKW-3, and K-562) and showed to have potent cytotoxic agent with IC_{50} value between 3.42-5.87 µM.[35]

Compounds **58-61** are derivatives of the genus *Hypericum* and characterized by having the substituent R_1 as an alkyl chain, R_2 varying between prenyl or geranyl, and R_3 being methyl or geranyl (Figures 5 and 10; Tables 1-2).

The acylphloroglucinol **58** was obtained from petroleum ether extracts of the aerial parts of the species *H. calycinum* and showed antifungal and antimalarial action against *C. cucumerinum* and *P. falciparum*, respectively.[40] The geranylated compound **59** proved to be a potent antibacterial agent against *S. aureus* and *B. subtilis* and was obtained from the methanolic extracts of *H. erectum*.[79] Compounds **60-61** were isolated by extracting the aerial parts of *H. empetrifolium* in petroleum ether.[3]

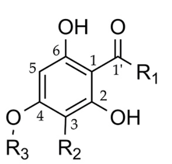
Regarding metabolites **62-64** (Figures 5 and 11; Tables 1-2), compound **62** was obtained from the polar fractions of a chloroform extract of the rhizome of *Remirea maritima*;[49] compounds **63-64**, both geranylated, were found in the species *Hypericum empetrifolium* and isolated from petroleum ether extracts of aerial parts.[3]

Compounds **65-77** are subdivided into the genera *Hypericum* and *Acronychia* (Figures 5 and 12; Tables 1-2): As for the first genus, prenylates **66-67** were isolated from *H. laricifolium* (hexane), **68** from *H. foliosum* (hexane), and **74** from *H. empetrifolium* (petroleum ether), all from aerial parts of the species.[3,85,86] In addition, an antimicrobial action against *S. aureus* was associated with **68**.[86] Regarding prenylated compounds of the genus *Acronychia*, **69-71**, **73**, and **75-77** were obtained from ethanolic extracts (95%) of *A. oligophlebia* leaves, in which **70-71**, **73**, and **75** were found to exhibit cytotoxic activity against MCF-7 cells with IC_{50} values of 56.8 (for the last three compounds).[87,88] Furthermore, **65** and **72** were extracted from methanolic extracts of leaves of *A. pedunculata*, and the latter being tested for its cytotoxic activity on deoxyribonucleic acid (DNA) polymerases and human cancer cells.[50,83]

Derivatives **78-88** exhibit a wide range of variant substituents between groups such as prenyl and geranyl (Figures 5 and 13; Tables 1-2). Geranylated metabolites **78-80** were isolated from *H. japonicum* in different extracts: 95% ethanol (**78-79**, cytotoxic against HT22) and hexane (**80**).[68,89] Compounds **81** (stems and roots, CH_3OH), **86** (stem, bark, CH_3OH), **87** (leaves, CH_2Cl_2), and **88** (stems and roots, CH_3OH) were obtained from *A. pedunculata*.[82,84,90] Compounds **82-83** were associated with ethanolic extracts from the roots of *L. pulverulenta*, and **84** obtained from *M. barbigera* leaf extracts in CH_2Cl_2, while **85** was isolated from *L. squarrosus* (aerial parts, ether/petroleum ether extract).[41,91,92]

4.2. Bicyclic and tricyclic acylphloroglucinol derivatives

Polycyclic derivatives **89-139** were grouped according



51 R_1= CH_2OH, R_2= R_3= Prenyl
52 R_1= CH_3, R_2= R_3= Prenyl
53 R_1= R_3= CH_3, R_2= Prenyl
54 R_1= CH_3, R_2= Prenyl, R_3= Geranyl (*trans*)
55 R_1= $CH(CH_3)_2$, R_2= CH_3, R_3= Geranyl (*trans*)
56 R_1= CH_2OH, R_2= Prenyl, R_3= Geranyl (*trans*)
57 R_1= $CH(CH_3)_2$, R_3= H, R_2=

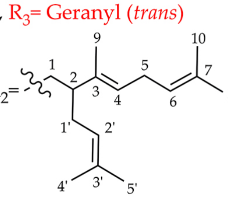
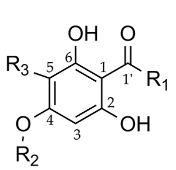
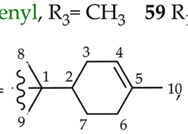


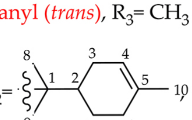
Figure 9. Monocyclic monomeric derivatives of acylphloroglucinols **51-57**.



58 R_1= $CH_2CH(CH_3)_2$, R_2= Prenyl, R_3= CH_3
59 R_1= $CH(CH_3)CH_2CH_3$, R_2= Geranyl (*trans*), R_3= CH_3
60 R_1= $CH(CH_3)CH_2CH_3$, R_2=

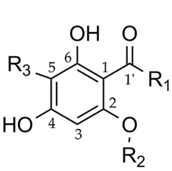


R_3= Geranyl (*trans*)
61 R_1= $CH(CH_3)_2$, R_2=

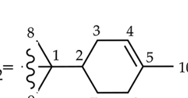


R_3= Geranyl (*trans*)

Figure 10. Monocyclic monomeric derivatives of acylphloroglucinols **58-61**.



62 R_1= R_2= CH_3, R_3= Prenyl
63 R_1= $CH(CH_3)_2$, R_3= Geranyl (*trans*), R_2=



64 R_1= $CH(CH_3)CH_2CH_3$, R_3= Geranyl (*trans*), R_2=

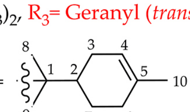


Figure 11. Monocyclic monomeric derivatives of acylphloroglucinols **62-64**.

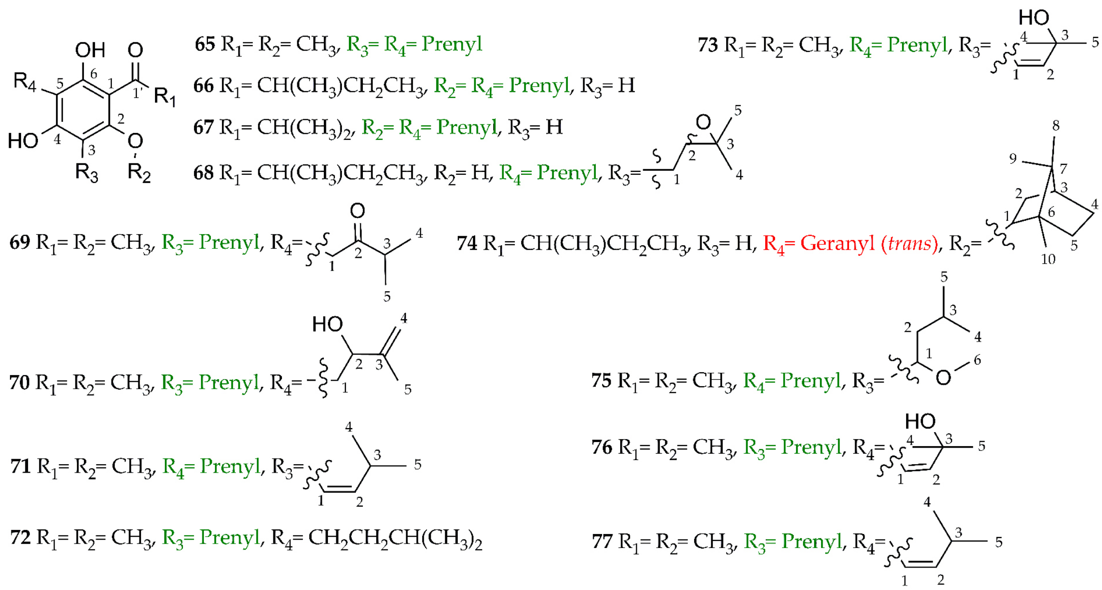


Figure 12. Monocyclic monomeric derivatives of acylphloroglucinols **65**-**77**.

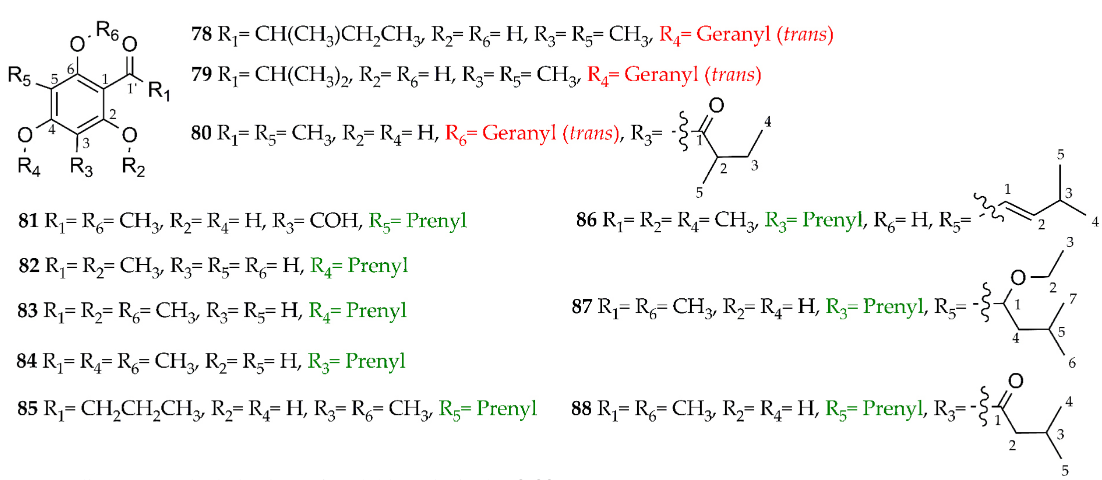


Figure 13. Monocyclic monomeric derivatives of acylphloroglucinols **78**-**88**.

to the structural similarity of the THB core (Figures 14 and 15; Tables 1 and 3).

Considering the genus *Helichrysum*, **89**, **91**, and **100** were obtained from *H. bellum* (aerial parts in petroleum ether) and **109** from *H. cerastioides* (aerial parts in a 1:3 ether/petroleum ether).[58,72] From the genus *Hypericum*, **90** was isolated from aerial parts, in CH_2Cl_2, from *H. lissophloeus*, and proved to be a potent stimulator of gamma-aminobutyricacid (GABA)-induced currents in recombinant $\alpha_1\beta_2\gamma_2$; compounds **94** and **130** were isolated from *H. japonicum* in CH_3CH_2OH/H_2O; a sequential extraction ($CHCl_3$ and CH_3OH) of the leaves of *H. roeperianum* resulted in the isolation of **95**; from aerial parts of *H. annulatum* in hexane, **96-97** and **137** were obtained.[35,65,93] Acylphloroglucinols **98-99** and **115-116** were associated with the prospection of *H. empetrifolium* (aerial parts in petroleum ether), and the last two compounds showed *in vitro* antiproliferative activity against human microvascular endothelial cells (HMEC-1) with IC_{50} values from 9.2 ± 2.0 to 29.6 ± 3.5 µM.[97] Extractions using petroleum ether, diethyl ether, CH_3OH and 1:1 CH_3OH/water of the aerial parts from *H. amblycalyx* allowed the isolation of phenolic derivatives **101-104**, which demonstrated antiproliferative activity against HMEC-1 with IC_{50} values identical to those **115-116**. Further, **103** and **104** showed moderate cytotoxicity against KB (human epithelial) and Jurkat T (T lymphocyte) cancer cells.[45,62,97,98] Compound **110** was obtained from aerial parts of *H. jovis* in petroleum ether.[45] Compound **111** was isolated from *H. prolificum* (aerial parts in hexane) and was able to inhibit proliferation of MCF-7 (human breast), NCI-H460 (lung), SF-268 (CNS), AGS (stomach) and HCT-116 (colon) tumor cell lines *in vitro*, with IC_{50}

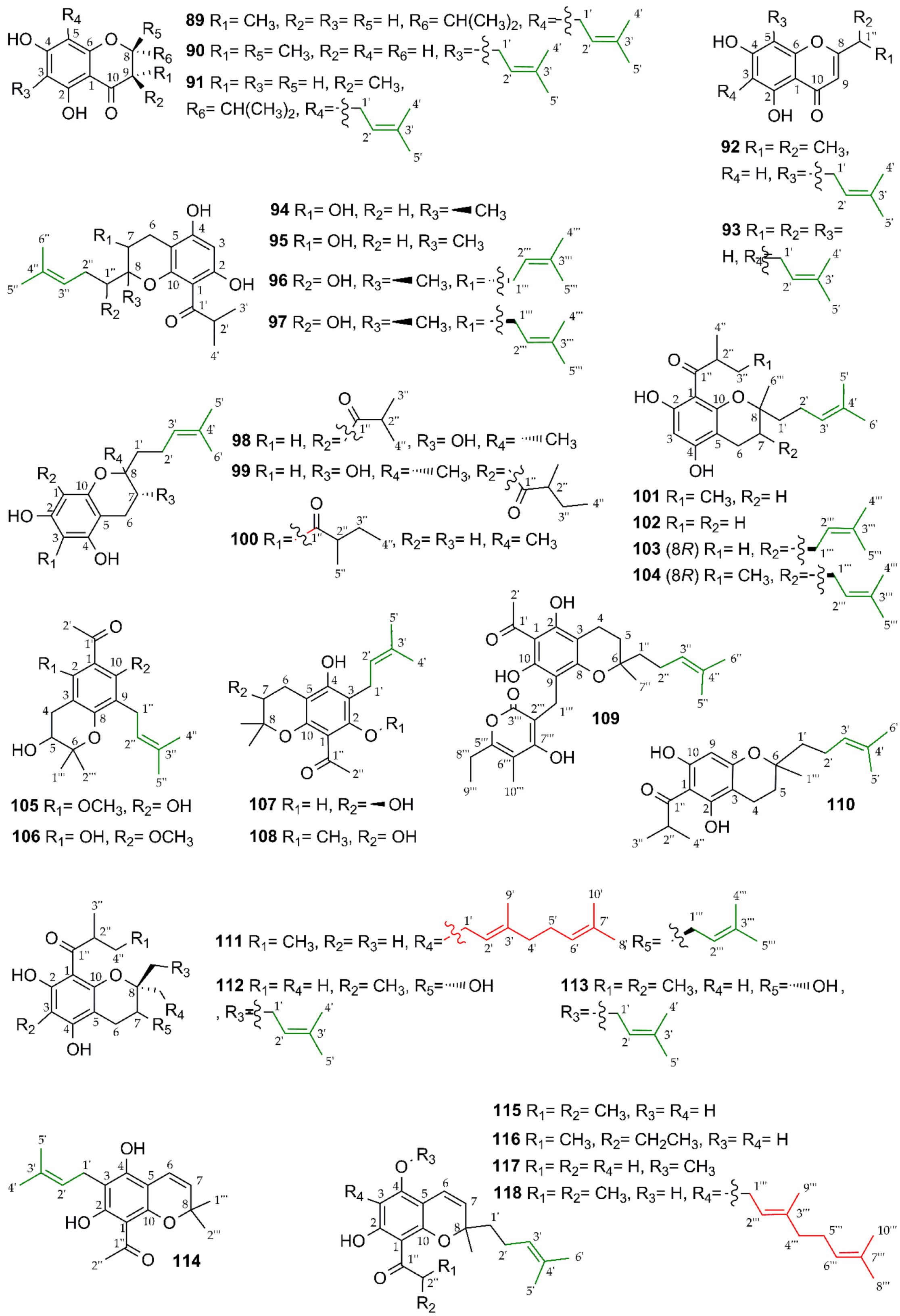


Figure 14. Bicyclic and tricyclic acylphloroglucinol derivatives **89-118**.

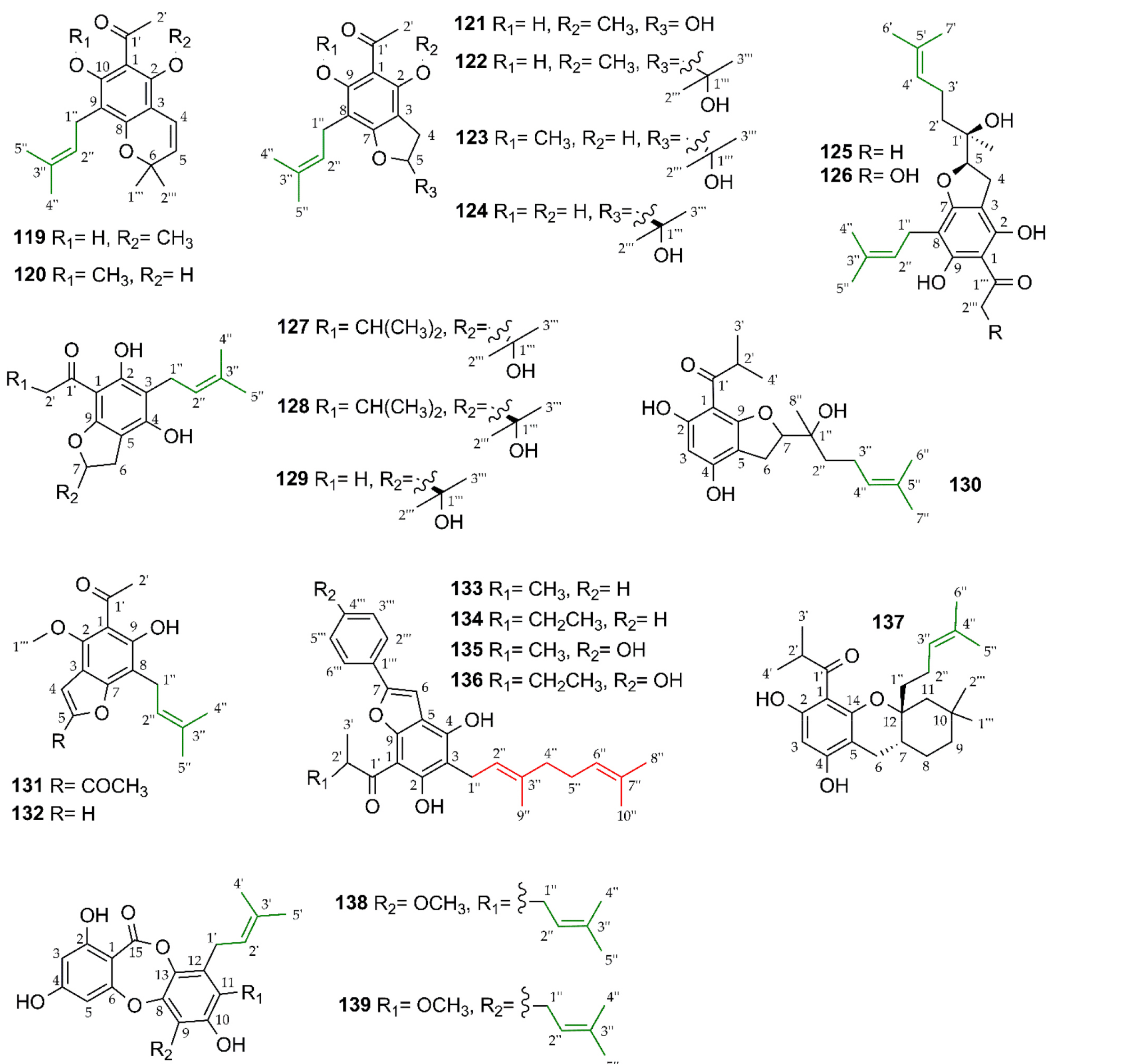


Figure 15. Bicyclic and tricyclic acylphloroglucinol derivatives **119-139**.

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
2β-Isopropyl-3β-methyl-8-(3',3'-dimethylallyl)-5,7-dihydroxychroman-4-one (**89**) $C_{18}H_{24}O_4$	*Helichrysum bellum* South Africa[58]	^{1}H NMR (270 MHz, $CDCl_3$) δ 5.98 (H-3), 3.91 (H-8), 2.73 (H-9), 1.20 (CH_3-9), 3.34 (H-1'), 5.24 (H-2'), 1.75 (H-4'), 1.80 (H-5'), 2.04 (H-1''), 1.15 (H-2''), 1.03 (H-3''), 12.07 (OH)[58]
((2*R*,3*R*)-5,7-Dihydroxy-2,3-dimethyl-6-(3-methyl-but-2-en-1-yl)-chroman-4-one (**90**) $C_{16}H_{20}O_4$	*Hypericum lissophloeus* United States[93]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (H-5), 4.16 (H-8), 2.56 (H-9), 3.33 (H-1'), 5.24 (H-2'), 1.80 (H-4'), 1.76 (H-5'), 1.48 (H-1''), 1.22 (H-2''), 12.50 (OH-2), 6.16 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 102.1 (C-1), 161.2 (C-2), 106.6 (C-3), 163.4 (C-4), 95.0 (C-5), 160.8 (C-6), 78.8 (C-8), 45.8 (C-9), 198.8 (C-10), 21.2 (C-1'), 121.6 (C-2'), 135.4 (C-3'), 17.9 (C-4'), 25.8 (C-5'), 19.6 (C-1''), 10.3 (C-2'')[93]
2β-Isopropyl-3α-methyl-8-(3',3'-dimethylallyl)-5,7-dihydroxychroman-4-one (**91**) $C_{18}H_{24}O_4$	*Helichrysum bellum* South Africa[58]	^{1}H NMR (270 MHz, $CDCl_3$) δ 5.99 (H-3), 3.83 (H-8), 2.60 (H-9), 1.20 (CH_3-9), 3.33 (H-1'), 5.24 (H-2'), 1.75 (H-4'), 1.80 (H-5'), 2.05 (H-1''), 1.14 (H-2''), 1.03 (H-3''), 12.0 (OH)[58]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
5,7-Dihydroxy-2-isopropyl-8-prenylchromone (**92**) $C_{17}H_{20}O_4$	*Humulus lupulus* China[94]	^{1}H NMR (400 MHz, DMSO-d_6) δ 6.26 (H-3), 6.12 (H-9), 3.31 (H-1'), 5.15 (H-2'), 1.74 (H-4'), 1.62 (H-5'), 2.90 (H-1''), 1.25 (H-2'' H-3''), 12.73 (OH-2), 10.71 (OH-4) ^{13}C NMR (100 MHz, DMSO-d_6) δ 103.5 (C-1), 159.0 (C-2), 98.2 (C-3), 161.5 (C-4), 105.9 (C-5), 154.9 (C-6), 174.5 (C-8), 105.0 (C-9), 182.3 (C-10), 21.1 (C-1'), 122.3 (C-2'), 130.7 (C-3'), 17.7 (C-4'), 25.4 (C-5'), 32.5 (C-1''), 19.7 (C-2'' C-3'')[94]
Peucenin (**93**) $C_{15}H_{16}O_4$	*Harrisonia abyssinica* Nigeria[95]	^{1}H NMR[a] ($CDCl_3$) δ 6.30, 5.95, 5.30, 3.42, 2.34, 1.82, 1.78[95]
(±)-Japonicol F (**94**) $C_{20}H_{28}O_5$	*Hypericum japonicum* China[96]	^{1}H NMR (400 MHz, CD_3OD) δ 2.85 (H-6), 2.45 (H-6), 3.86 (H-7), 3.95 (H-2'), 1.13 (H-3'), 1.15 (H-4'), 1.80 (H-1''), 1.72 (H-1''), 2.20 (H-2''), 2.16 (H-2''), 5.14 (H-3''), 1.62 (H-5''), 1.69 (H-6''), 1.27 (H-1''') ^{13}C NMR (100 MHz, CD_3OD) δ 164.3 (C-4), 101.5 (C-5), 26.8 (C-6), 67.2 (C-7), 81.6 (C-8), 157.2 (C-10), 211.0 (C-1'), 40.1 (C-2'), 19.9 (C-3'), 20.4 (C-4'), 39.1 (C-1''), 23.2 (C-2''), 125.1 (C-3''), 132.8 (C-4''), 17.9 (C-5''), 26.0 (C-6''), 18.7 (C-1''')[96]
Madeleinol B (**95**) $C_{20}H_{28}O_5$	*Hypericum roeperianum* Cameroon[65] *Hypericum jovis* Greece[62]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (H-3), 3.85 (H-2'), 1.18 (H-3' H-4'), 2.60 (H-6), 2.89 (H-6), 3.95 (H-7), 1.71 (H-1''), 1.77 (H-1''), 2.25 (H-2''), 5.09 (H-3''), 1.69 (H-5''), 1.60 (H-6''), 1.38 (H-7''), 13.81 (OH-2), 5.43 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.4 (C-1), 165.7 (C-2), 96.3 (C-3), 159.8 (C-4), 97.9 (C-5), 25.2 (C-6), 66.4 (C-7), 80.7 (C-8), 155.7 (C-10), 210.4 (C-1'), 39.4 (C-2'), 19.2 (C-3'), 19.7 (C-4'), 37.5 (C-1''), 22.0 (C-2''), 123.4 (C-3''), 132.6 (C-4''), 25.7 (C-5''), 17.6 (C-6''), 19.0 (C-7'')[65]
Hyperannulatin D (**96**) $C_{25}H_{36}O_5$	*Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.98 (H-3), 2.75 (H-6), 2.21 (H-6), 2.04 (H-7), 3.94 (H-2'), 1.16 (H-3'), 1.17 (H-4'), 1.36 (H-5'), 3.79 (H-1''), 2.35 (H-2''), 5.19 (H-3''), 1.75 (H-5''), 1.64 (H-6''), 2.20 (H-1'''), 1.86 (H-1'''), 5.14 (H-2'''), 1.72 (H-4'''), 1.59 (H-5'''), 13.95 (OH-2) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.3 (C-1), 165.3 (C-2), 96.0 (C-3), 160.2 (C-4), 100.4 (C-5), 22.0 (C-6), 35.5 (C-7), 83.1 (C-8), 156.3 (C-10), 210.6 (C-1'), 39.2 (C-2'), 20.3 (C-3'), 19.2 (C-4'), 15.7 (C-5'), 74.1 (C-1''), 29.9 (C-2''), 120.4 (C-3''), 136.4 (C-4''), 26.1 (C-5''), 18.1 (C-6''), 28.8 (C-1'''), 121.7 (C-2'''), 133.8 (C-3'''), 26.0 (C-4'''), 18.1 (C-5''')[35]
Hyperannulatin E (**97**) $C_{25}H_{36}O_5$	*Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99 (H-3), 2.59 (H-6), 2.51 (H-6), 2.02 (H-7), 3.81 (H-2'), 1.15 (H-3'), 1.16 (H-4'), 1.37 (H-5'), 3.88 (H-1''), 2.32 (H-2''), 5.18 (H-3''), 1.76 (H-5''), 1.66 (H-6''), 2.39 (H-1'''), 1.93 (H-1'''), 5.13 (H-2'''), 1.70 (H-4'''), 1.49 (H-5'''), 13.91 (OH-2) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.1 (C-1), 165.3 (C-2), 96.2 (C-3), 160.6 (C-4), 99.8 (C-5), 20.8 (C-6), 37.3 (C-7), 82.0 (C-8), 156.0 (C-10), 210.3 (C-1'), 39.5 (C-2'), 19.8 (C-3'), 19.3 (C-4'), 18.7 (C-5'), 72.6 (C-1''), 30.9 (C-2''), 120.4 (C-3''), 136.7 (C-4''), 26.2 (C-5''), 18.2 (C-6''), 27.2 (C-1'''), 122.9 (C-2'''), 133.8 (C-3'''), 26.0 (C-4'''), 17.9 (C-5''')[35]
Empetrikarinol A (**98**) $C_{20}H_{28}O_5$	*Hypericum empetrifolium* Greece[97]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.86 (H-3), 2.48 (H-6), 2.76 (H-6), 3.84 (H-7), 1.58 (H-1'), 1.66 (H-1'), 2.02 (H-2'), 4.97 (H-3'), 1.57 (H-5'), 1.48 (H-6'), 3.73 (H-2''), 1.06 (H-3'' H-4''), 1.27 (CH_3-8), 13.78 (OH-2), 5.91 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.2 (C-1), 165.5 (C-2), 96.2 (C-3), 160.2 (C-4), 97.9 (C-5), 25.5 (C-6), 66.4 (C-7), 80.6 (C-8), 155.7 (C-10), 37.4 (C-1'), 22.0 (C-2'), 123.4 (C-3'), 132.5 (C-4'), 25.6 (C-5'), 17.6 (C-6'), 210.3 (C-1''), 39.3 (C-2''), 19.2 (C-3''), 19.6 (C-4''), 19.0 (CH_3-8)[97]
Empetrikarinol B (**99**) $C_{21}H_{30}O_5$	*Hypericum empetrifolium* Greece[97] *Hypericum roeperianum* Cameroon[65] *Garcinia dauphinensis* Madagascar[66]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.96 (H-3), 2.62 (H-6), 2.86 (H-6), 3.94 (H-7), 1.68 (H-1'), 1.75 (H-1'), 2.12 (H-2'), 5.08 (H-3'), 1.67 (H-5'), 1.58 (H-6'), 3.75 (H-2''), 1.40 (H-3''), 1.80 (H-3''), 0.89 (H-4''), 1.15 (H-5''), 1.39 (CH_3-8), 13.99 (OH-2), 6.48 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.7 (C-1), 165.3 (C-2), 96.2 (C-3), 160.5 (C-4), 98.1 (C-5), 25.5 (C-6), 66.4 (C-7), 80.5 (C-8), 155.7 (C-10), 37.3 (C-1'), 22.0 (C-2'), 123.3 (C-3'), 132.5 (C-4'), 25.6 (C-5'), 17.6 (C-6'), 210.4 (C-1''), 46.1 (C-2''), 26.9 (C-3''), 11.7 (C-4''), 16.5 (C-5''), 19.3 (CH_3-8)[97]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
1-(5,7-Dihydroxy-2-methyl-2-(4-methylpent-3-enyl)chroman-6-yl)-2-methyl-butan-1-one (**100**) $C_{21}H_{30}O_4$	*Helichrysum bellum* South Africa[58] *Hypericum empetrifolium* Greece[97] *Garcinia dauphinensis* Madagascar[66]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (H-1), 2.56 (H-6), 1.75 (H-7), 1.83 (H-7), 1.61 (H-1’), 2.06 (H-2’), 5.08 (H-3’), 1.67 (H-5’), 1.60 (H-6’), 3.73 (H-2’’), 1.40 (H-3’’), 1.84 (H-3’’), 0.91 (H-4’’), 1.15 (H-5’’), 1.29 (CH_3-8), 6.19 (OH-2), 13.61 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 95.6 (C-1), 157.4 (C-2), 103.7 (C-3), 163.9 (C-4), 101.9 (C-5), 15.8 (C-6), 30.2 (C-7), 77.8 (C-8), 160.1 (C-10), 39.4 (C-1’), 22.2 (C-2’), 123.9 (C-3’), 131.8 (C-4’), 25.6 (C-5’), 17.6 (C-6’), 209.9 (C-1’’), 45.8 (C-2’’), 26.9 (C-3’’), 11.9 (C-4’’), 16.7 (C-5’’), 24.0 (CH_3-8)[97]
1-(5,7-Dihydroxy-2-methyl-2-(4-methyl-pent-3-enyl)-chroman-8-yl)-2-methyl-butan-1-one (**101**) $C_{21}H_{30}O_4$	*Hypericum amblycalyx* Greece[98] *Hypericum empetrifolium* Greece[97] *Hypericum jovis* Greece[62]	^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (H-3), 2.59 (H-6), 1.83 (H-7), 1.36 (CH_3-8), 1.71 (H-1’), 2.09 (H-2’), 5.10 (H-3’), 1.61 (H-5’), 1.69 (H-6’), 3.77 (H-2’’), 1.43 (H-3’’), 1.83 (H-3’’), 0.90 (H-4’’), 1.16 (H-5’’), 14.06 (OH) ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.0 (C-1), 165.0 (C-2), 95.4 (C-3), 160.1 (C-4), 99.9 (C-5), 16.1 (C-6), 29.1 (C-7), 78.3 (C-8), 157.0 (C-10), 23.9 (CH_3-8), 39.6 (C-1’), 22.5 (C-2’), 123.6 (C-3’), 132.1 (C-4’), 17.6 (C-5’), 25.7 (C-6’), 210.6 (C-1’’), 45.8 (C-2’’), 26.4 (C-3’’), 11.8 (C-4’’), 16.6 (C-5’’)[98]
1-(5,7-Dihydroxy-2-methyl-2-(4-methyl-pent-3-enyl)-chroman-8-yl)-2-methyl-propan-1-one (**102**) $C_{20}H_{28}O_4$	*Hypericum amblycalyx* Greece[98] *Hypericum jovis* Greece[45,62] *Hypericum empetrifolium* Greece[97]	^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 (H-3), 2.61 (H-6), 1.78 (H-7), 1.88 (H-7), 1.36 (CH_3-8), 1.72 (H-1’), 2.10 (H-2’), 5.11 (H-3’), 1.62 (H-5’), 1.70 (H-6’), 3.87 (H-2’’), 1.18 (H-3’’ H-4’’), 13.96 (OH) ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.4 (C-1), 165.2 (C-2), 95.4 (C-3), 159.9 (C-4), 99.7 (C-5), 16.1 (C-6), 29.1 (C-7), 78.7 (C-8), 156.9 (C-10), 23.8 (CH_3-8), 39.8 (C-1’), 22.6 (C-2’), 123.6 (C-3’), 132.1 (C-4’), 17.6 (C-5’), 25.7 (C-6’), 210.6 (C-1’’), 39.8 (C-2’’), 19.2 (C-3’’), 19.7 (C-4’’)[98]
Hypercalyxone A (**103**) $C_{25}H_{36}O_4$	*Hypericum amblycalyx* Greece[97] *Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (H-3), 2.14 (H-6), 2.73 (H-6), 1.92 (H-7), 1.25 (CH_3-8), 1.82 (H-1’), 2.14 (H-2’), 5.11 (H-3’), 1.62 (H-5’), 1.70 (H-6’), 3.79 (H-2’’), 1.41 (H-3’’), 1.82 (H-3’’), 0.90 (H-4’’), 1.15 (H-5’’), 1.82 (H-1’’’), 2.24 (H-1’’’), 5.18 (H-2’’’), 1.63 (H-4’’’), 1.74 (H-5’’’), 13.87 (OH) ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.0 (C-1), 165.1 (C-2), 95.5 (C-3), 159.7 (C-4), 100.1 (C-5), 21.7 (C-6), 35.9 (C-7), 81.3 (C-8), 156.8 (C-10), 20.2 (CH_3-8), 39.3 (C-1’), 21.7 (C-2’), 123.6 (C-3’), 132.1 (C-4’), 17.7 (C-5’), 25.7 (C-6’), 210.4 (C-1’’), 45.7 (C-2’’), 26.9 (C-3’’), 11.8 (C-4’’), 16.6 (C-5’’), 29.0 (C-1’’’), 121.7 (C-2’’’), 133.5 (C-3’’’), 17.9 (C-4’’’), 25.9 (C-5’’’)[98]
Hypercalyxone B (**104**) $C_{26}H_{38}O_4$	*Hypericum amblycalyx* Greece[98]	^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (H-3), 2.14 (H-6), 2.73 (H-6), 1.92 (H-7), 1.24 (CH_3-8), 1.82 (H-1’), 2.13 (H-2’), 5.11 (H-3’), 1.62 (H-5’), 1.71 (H-6’), 3.87 (H-2’’), 1.17 (H-3’’), 1.18 (H-4’’), 1.82 (H-1’’’), 2.25 (H-1’’’), 5.18 (H-2’’’), 13.87 (OH) ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.4 (C-1), 165.2 (C-2), 95.5 (C-3), 159.7 (C-4), 100.0 (C-5), 21.8 (C-6), 36.0 (C-7), 81.4 (C-8), 156.7 (C-10), 20.0 (CH_3-8), 39.4 (C-1’), 21.8 (C-2’), 123.7 (C-3’), 132.1 (C-4’), 17.6 (C-5’), 25.7 (C-6’), 210.5 (C-1’’), 39.2 (C-2’’), 19.2 (C-3’’), 19.8 (C-4’’), 29.0 (C-1’’’), 121.7 (C-2’’’), 133.5 (C-3’’’), 17.9 (C-4’’’), 25.9 (C-5’’’)[98]
Acronyculatin I (acrophenone D) (**105**) $C_{19}H_{26}O_5$	*Acronychia trifoliolata* Indonesia[53] *Acronychia pedunculata* Taiwan[51]	^{1}H NMR (600 MHz, $CDCl_3$) δ 2.72 (H-4), 2.97 (H-4), 3.83 (H-5), 2.68 (H-2’), 3.29 (H-1’’), 5.22 (H-2’’), 1.79 (H-4’’), 1.67 (H-5’’), 1.37 (H-1’’’ H-2’’’), 3.75 (CH_3-2), 1.70 (OH), 13.25 (OH) ^{13}C NMR (150 MHz, $CDCl_3$) δ 109.3 (C-1), 159.7 (C-2), 104.3 (C-3), 26.2 (C-4), 69.2 (C-5), 77.8 (C-6), 157.4 (C-8), 113.2 (C-9), 161.1 (C-10), 203.3 (C-1’), 31.1 (C-2’), 21.7 (C-1’’), 122.2 (C-2’’), 131.4 (C-3’’), 17.9 (C-4’’), 25.8 (C-5’’), 21.9 (C-1’’’), 25.2 (C-2’’’), 61.5 (OCH_3-2)[53]
Acronyculatin K (**106**) $C_{19}H_{26}O_5$	*Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (600 MHz, $CDCl_3$) δ 3.26 (H-4), 5.14 (H-5), 2.69 (H-2’), 2.69 (H-1’’), 2.90 (H-1’’), 3.84 (H-2’’), 1.32 (H-4’’), 1.37 (H-5’’), 1.77 (H-1’’’), 1.68 (H-2’’’), 3.72 (OCH_3-10), 1.61 (OH), 13.60 (OH)[53]
Selwynone (**107**) $C_{18}H_{24}O_5$	*Bosistoa selwyni* Australia[99]	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (H-6), 2.87 (H-6), 3.80 (H-7), 1.35 (CH_3-8), 1.40 (CH_3-8), 3.40 (H-1’), 5.27 (H-2’), 1.68 (H-4’), 1.61 (H-5’), 2.60 (H-2’’), 14.07 (OH-2), 6.30 (OH-4) ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.0 (C-1), 162.7 (C-2), 105.5 (C-3), 160.3 (C-4), 97.8 (C-5), 22.1 (C-6), 69.9 (C-7), 78.3 (C-8), 154.4 (C-9), 25.0 (CH_3-8), 22.2 (CH_3-8), 26.1 (C-1’), 122.0 (C-2’), 135.5 (C-3’), 26.0 (C-4’), 18.1 (C-5’), 203.5 (C-1’’), 33.6 (C-2’’)[99]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^1H and ^{13}C NMR data (chemical shift δ / ppm)
Acronyculatin L (**108**) (acrophenone C) $C_{19}H_{26}O_5$	*Acronychia trifoliolata* Indonesia[53] *Acronychia pedunculata* Taiwan[100]	^1H NMR (600 MHz, $CDCl_3$) δ 3.35 (H-6), 5.22 (H-7), 2.65 (H-1'), 2.87 (H-1'), 3.80 (H-2'), 1.32 (H-4'), 1.34 (H-5'), 2.49 (H-2''), 3.71 (OCH_3-2), 1.79 (CH_3-8), 1.85 (CH_3-8), 5.74 (OH)[53]
Helicerastripyron (**109**) $C_{27}H_{34}O_7$	*Helichrysum cerastioides* South Africa[72]	^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (H-4), 5.40 (H-5), 2.68 (H-2'), 1.85 (H-1''), 2.10 (H-2''), 5.09 (H-3''), 1.66 (H-5''), 1.55 (H-6''), 1.42 (H-7''), 3.63 (H-1'''), 2.56 (H-8'''), 1.19 (H-9'''), 1.95 (H-10''')[72]
1-(5,7-Dihydroxy-2-methyl-2-(4-methylpent-3-enyl)chroman-6-yl)-2-methyl-propan-1-one (**110**) $C_{20}H_{28}O_4$	*Hypericum jovis* Greece[45,62] *Hypericum empetrifolium* Greece[97]	^1H NMR (600 MHz, $CDCl_3$) δ 2.56 (H-4), 1.75 (H-5), 1.82 (H-5), 5.72 (H-9), 1.61 (H-1'), 2.06 (H-2'), 5.08 (H-3'), 1.67 (H-5'), 1.59 (H-6'), 3.86 (H-2''), 1.17 (H-3'' H-4''), 1.28 (H-1'''), 13.55 (OH-2), 6.14 (OH-10) ^{13}C NMR (150 MHz, $CDCl_3$) δ 103.1 (C-1), 164.0 (C-2), 101.9 (C-3), 15.8 (C-4), 30.2 (C-5), 77.7 (C-6), 160.1 (C-8), 95.6 (C-9), 157.3 (C-10), 39.3 (C-1'), 22.2 (C-2'), 123.9 (C-3'), 131.8 (C-4'), 25.6 (C-5'), 17.6 (C-6'), 210.1 (C-1''), 39.1 (C-2''), 19.2 (C-3'' C-4''), 24.0 (C-1''')[97]
Prolificin A (**111**) $C_{31}H_{46}O_4$	*Hypericum prolificum* United States[101] *Hypericum* spp. United States[64]	^1H NMR (400 MHz, Benzene-d_6) δ 5.82 (H-3), 2.81 (H-6), 2.15 (H-6), 1.75 (H-7), 1.68 (CH_2-8), 0.98 (CH_3-8), 2.06 (H-1'), 5.17 (H-2'), 2.06 (H-4'), 2.05 (H-5'), 2.18 (H-5'), 5.24 (H-6'), 1.71 (H-8'), 1.55 (H-9'), 1.59 (H-10'), 3.94 (H-2''), 1.27 (H-3''), 1.49 (H-4''), 1.98 (H-4''), 0.93 (H-5''), 1.68 (H-1'''), 2.10 (H-1'''), 5.13 (H-2'''), 1.66 (H-4'''), 1.56 (H-5'''), 14.7 (OH-2), 5.08 (OH-4) ^{13}C NMR (100 MHz, Benzene-d_6) δ 106.2 (C-1), 166.2 (C-2), 95.9 (C-3), 160.2 (C-4), 100.3 (C-5), 22.2 (C-6), 36.0 (C-7), 81.0 (C-8), 156.8 (C-10), 39.4 (CH_2-8), 19.8 (CH_3-8), 21.9 (C-1'), 122.3 (C-2'), 136.5 (C-3'), 40.0 (C-4'), 26.8 (C-5'), 124.5 (C-6'), 131.2 (C-7'), 25.63 (C-8'), 16.0 (C-9'), 17.54 (C-10'), 210.0 (C-1''), 45.9 (C-2''), 27.2 (C-3''), 11.8 (C-4''), 16.8 (C-5''), 29.1 (C-1'''), 124.1 (C-2'''), 131.5 (C-3'''), 25.57 (C-4'''), 17.45 (C-5''')[101]
Petiolin J (**112**) $C_{21}H_{30}O_5$	*Hypericum pseudopetiolatum* Japan[102]	^1H NMR[a] ($CDCl_3$) δ 2.91 (H-6), 2.62 (H-6), 3.96 (H-7), 1.71 (CH_2-8), 1.78 (CH_2-8), 1.37 (CH_3-8), 2.12 (CH_3-3), 2.14 (H-1'), 5.01 (H-2'), 1.61 (H-4'), 1.69 (H-5'), 3.88 (H-2''), 1.18 (H-3'' H-4''), 14.17 (OH-2) ^{13}C NMR[a] ($CDCl_3$) δ 105.0 (C-1), 163.3 (C-2), 7.1 (CH_3-3), 102.2 (C-3), 157.9 (C-4), 97.1 (C-5), 25.8 (C-6), 66.5 (C-7), 80.2 (C-8), 153.3 (C-10), 37.4 (CH_2-8), 18.9 (CH_3-8), 22.0 (C-1'), 123.5 (C-2'), 132.5 (C-3'), 17.6 (C-4'), 25.7 (C-5'), 210.6 (C-1''), 39.4 (C-2''), 19.3 (C-3''), 19.8 (C-4'')[102]
Yojironin D (**113**) $C_{22}H_{32}O_5$	*Hypericum yojiroanum* Japan[103]	^1H NMR[a] ($CDCl_3$) δ 2.90 (H-6), 2.61 (H-6), 3.94 (H-7), 1.69 (CH_2-8), 1.77 (CH_2-8), 1.37 (CH_3-8), 2.13 (H-1'), 5.08 (H-2'), 1.59 (H-4'), 1.68 (H-5'), 3.77 (H-2''), 1.16 (H-3''), 1.81 (H-4''), 1.42 (H-4''), 0.89 (H-5''), 14.14 (OH-2) ^{13}C NMR[a] ($CDCl_3$) δ 105.7 (C-1), 163.2 (C-2), 102.3 (C-3), 157.8 (C-4), 97.2 (C-5), 25.9 (C-6), 66.5 (C-7), 80.2 (C-8), 153.3 (C-10), 37.3 (CH_2-8), 19.1 (CH_3-8), 22.0 (C-1'), 123.5 (C-2'), 132.5 (C-3'), 17.5 (C-4'), 25.6 (C-5'), 210.6 (C-1''), 46.0 (C-2''), 16.7 (C-3''), 27.1 (C-4''), 11.8 (C-5'')[103]
8-Acetyl-5,7-dihydroxy-6-isopentenyl-2,2-dimethyl-2*H*-1-benzopyran (**114**) $C_{18}H_{22}O_4$	*Melicope ptelefolia* Vietnam[104]	^1H NMR (300 MHz, $CDCl_3$) δ 6.54 (H-6), 5.54 (H-7), 3.39 (H-1'), 5.27 (H-2'), 1.78 (H-4'), 1.84 (H-5'), 2.67 (H-2''), 1.49 (1''' 2'''), 14.13 (OH-2), 6.32 (OH-4) ^{13}C NMR (75 MHz, $CDCl_3$) δ 105.8 (C-1), 162.9 (C-2), 105.2 (C-3), 157.4 (C-4), 101.9 (C-5), 116.5 (C-6), 124.9 (C-7), 77.8 (C-8), 155.3 (C-10), 21.5 (C-1'), 121.7 (C-2'), 136.6 (C-3'), 25.8 (C-4'), 17.9 (C-5'), 203.5 (C-1''), 33.2 (C-2''), 27.8 (C-1''' C-2''')[104]
Empetrikarinen A (**115**) $C_{20}H_{26}O_4$	*Hypericum empetrifolium* Greece[97]	^1H NMR (600 MHz, $CDCl_3$) δ 5.88 (H-3), 6.59 (H-6), 5.41 (H-7), 1.69 (H-1'), 1.86 (H-1'), 2.07 (H-2'), 2.15 (H-2'), 5.10 (H-3'), 1.67 (H-5'), 1.57 (H-6'), 3.85 (H-2''), 1.18 (H-3'' H-4''), 1.44 (H-1'''), 13.83 (OH-2), 5.38 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.2 (C-1), 166.2 (C-2), 96.1 (C-3), 157.2 (C-4), 101.5 (C-5), 116.8 (C-6), 123.2 (C-7), 80.9 (C-8), 156.8 (C-10), 41.5 (C-1'), 23.1 (C-2'), 123.6 (C-3'), 132.1 (C-4'), 25.6 (C-5'), 17.5 (C-6'), 210.4 (C-1''), 39.2 (C-2''), 19.2 (C-3''), 19.5 (C-4''), 26.5 (C-1''')[97]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
Empetrikarinen B (**116**) $C_{21}H_{28}O_4$	*Hypericum empetrifolium* Greece[97]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (H-3), 6.59 (H-6), 5.41 (H-7), 1.68 (H-1’), 1.87 (H-1’), 2.08 (H-2’), 2.15 (H-2’), 5.09 (H-3’), 1.67 (H-5’), 1.57 (H-6’), 3.75 (H-2’’), 1.41 (H-3’’), 1.86 (H-3’’), 0.91 (H-4’’), 1.16 (H-5’’), 1.44 (H-1’’’), 13.87 (OH-2), 5.40 (OH-4) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.8 (C-1), 166.2 (C-2), 96.1 (C-3), 157.1 (C-4), 101.5 (C-5), 116.8 (C-6), 123.3 (C-7), 80.9 (C-8), 156.8 (C-10), 41.6 (C-1’), 23.2 (C-2’), 123.6 (C-3’), 132.1 (C-4’), 25.6 (C-5’), 17.6 (C-6’), 210.3 (C-1’’), 46.0 (C-2’’), 26.8 (C-3’’), 11.8 (C-4’’), 17.1 (C-5’’), 26.5 (C-1’’’)[97]
Melibarbichromen A (**117**) $C_{19}H_{24}O_4$	*Melicope barbigera* United States[92]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99 (H-3), 6.59 (H-6), 5.38 (H-7), 1.79 (H-1’), 2.10 (H-2’), 5.09 (H-3’), 1.57 (H-5’), 1.66 (H-6’), 1.43 (H-7’), 2.66 (H-2’’), 3.83 (OCH_3-4), 13.84 (OH-2) ^{13}C NMR (150 MHz, $CDCl_3$) δ 106.0 (C-1), 166.7 (C-2), 91.9 (C-3), 161.2 (C-4), 102.7 (C-5), 116.8 (C-6), 123.0 (C-7), 80.9 (C-8), 156.7 (C-10), 41.7 (C-1’), 23.0 (C-2’), 123.6 (C-3’), 132.9 (C-4’), 25.9 (C-5’), 17.3 (C-6’), 26.7 (C-7’), 202.9 (C-1’’), 33.1 (C-2’’), 55.7 (OCH_3-4)[92]
Faberione E (**118**) $C_{30}H_{42}O_4$	*Hypericum faberi* China[67]	^{1}H NMR[a] ($CDCl_3$) δ 6.58 (H-6), 5.37 (H-7), 1.85 (H-1’), 1.65 (H-1’), 2.12 (H-2’), 2.04 (H-2’), 5.08 (H-3’), 1.65 (H-5’), 1.55 (H-6’), 3.86 (H-2’’), 1.17 (H-3’’), 1.16 (H-4’’), 3.39 (H-1’’’), 5.25 (H-2’’’), 2.07 (H-4’’’), 2.10 (H-5’’’), 5.02 (H-6’’’), 1.67 (H-8’’’), 1.79 (H-9’’’), 1.58 (H-10’’’), 14.28 (OH-2), 1.40 (CH_3-8), 6.33 (OH-4) ^{13}C NMR[a] ($CDCl_3$) δ 104.7 (C-1), 163.4 (C-2), 105.2 (C-3), 157.4(C-4), 101.7 (C-5), 117.3 (C-6), 123.2 (C-7), 80.5 (C-8), 154.9 (C-10), 41.6 (C-1’), 23.2 (C-2’), 123.8 (C-3’), 132.1 (C-4’), 25.8 (C-5’), 17.6 (C-6’), 210.7 (C-1’’), 39.3 (C-2’’), 19.4 (C-3’’), 19.7 (C-4’’), 21.6 (C-1’’’), 121.9 (C-2’’’), 140.3 (C-3’’’), 39.7 (C-4’’’), 26.1 (C-5’’’), 123.5 (C-6’’’), 132.4 (C-7’’’), 25.7 (C-8’’’), 16.2 (C-9’’’), 17.8 (C-10’’’), 26.5 (CH_3-8)[67]
Acronyculatin G (**119**) $C_{19}H_{24}O_4$	*Acronychia pedunculata* Thailand[83] *Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (H-4), 5.60 (H-5), 2.67 (H-2’), 3.28 (H-1’’), 5.21 (H-2’’), 1.67 (H-4’’), 1.79 (H-5’’), 1.44 (H-1’’’ H-2’’’), 3.77 (H-3’’’), 13.73 (OH-10) ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.6 (C-1), 157.0 (C-2), 106.8 (C-3), 117.0 (C-4), 127.9 (C-5), 77.2 (C-6), 158.0 (C-8), 113.2 (C-9), 163.5 (C-10), 203.2 (C-1’), 31.2 (C-2’), 21.5 (C-1’’), 122.2 (C-2’’), 131.3 (C-3’’), 25.8 (C-4’’), 17.9 (C-5’’), 28.2 (C-4’’’ C-5’’’), 63.0 (C-3’’’)[83]
Acronyculatin E (**120**) $C_{19}H_{24}O_4$	*Acronychia pedunculata* Thailand[83] Taiwan[51,90] *Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (H-4), 5.50 (H-5), 3.72 (OCH_3-10), 2.67 (H-2’), 3.23 (H-1’’), 5.15 (H-2’’), 1.77 (H-4’’), 1.68 (H-5’’), 1.43 (H-1’’’ H-2’’’), 13.52 (OH-2) ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.9 (C-1), 159.0 (C-2), 105.9 (C-3), 126.7 (C-4), 116.1 (C-5), 77.9 (C-6), 158.5 (C-8), 114.9 (C-9), 160.9 (C-10), 203.5 (C-1’), 30.9 (C-2’), 22.2 (C-1’’), 123.1 (C- 2’’), 131.3 (C-3’’), 17.9 (C-4’’), 25.7 (C-5’’), 28.3 (C-1’’’ 2’’’), 62.8 (OCH_3-10)[90]
Acronyculatin M (**121**) $C_{16}H_{20}O_5$	*Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (600 MHz, $CDCl_3$) δ 3.16 (H-4), 6.14 (H-5), 3.91 (OCH_3-2), 2.62 (H-2’), 3.26 (H-1’’), 5.24 (H-2’’), 1.76 (H-4’’), 1.67 (H-5’’), 3.18 (OH), 14.00 (OH) ^{13}C NMR (150 MHz, $CDCl_3$) δ 108.5 (C-1), 157.0 (C-2), 104.4 (C-3), 36.4 (C-4), 101.4 (C-5), 162.9 (C-7), 107.2 (C-8), 164.6 (C-9), 59.1 (CH_3-2), 203.3 (C-1’), 32.3 (C-2’), 22.2 (C-1’’), 121.8 (C-2’’), 132.1 (C-3’’), 17.8 (C-4’’), 25.8 (C-5’’)[53]
Acrophenone E (**122**) (acronyculatin B) $C_{19}H_{26}O_5$	*Acronychia pedunculata* Taiwan[51] *Acronychia trifoliolata* Indonesia[53]	^{1}H NMR[a] ($CDCl_3$) δ 3.34 (H-4), 4.69 (H-5), 2.57 (H-2’), 3.16 (H-1’’), 3.22 (H-1’’), 5.21 (H-2’’), 1.73 (H-4’’), 1.62 (H-5’’), 1.23 (H-2’’’), 1.24 (H-3’’’), 3.98 (H-4’’’), 3.81 (OH-5), 14.23 (OH-9). ^{13}C NMR[a] ($CDCl_3$) δ 108.3 (C-1), 157.8 (C-2), 108.3 (C-3), 29.4 (C-4), 91.3 (C-5), 166.5 (C-7), 106.3 (C-8), 165.1 (C-9), 203.7 (C-1’), 32.3 (C-2’), 22.6 (C-1’’), 123.1 (C-2’’), 131.4 (C-3’’), 17.8 (C-4’’), 25.0 (C-5’’), 71.5 (C-1’’’), 25.8 (C-2’’’), 26.3 (C-3’’’), 59.5 (C-4’’’)[51]
Acronyculatin B (acronyculatin O) (**123**) $C_{19}H_{26}O_5$	*Acronychia pedunculata* Taiwan[51,90] *Acronychia trifoliolata* Indonesia[53]	^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (H-4), 4.64 (H-5), 3.90 (H-OCH_3-9), 2.61 (H-2’), 3.22 (H-1’’), 5.24 (H-2’’), 1.76 (H-4’’), 1.67 (H-5’’), 1.36 (H-2’’’), 1.24 (H-3’’’), 14.52 (OH-2) ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.5 (C-1), 164.7 (C-2), 108.2 (C-3), 22.1 (C-4), 90.1 (C-5), 164.8 (C-7), 107.1 (C-8), 156.7 (C-9), 59.1 (OCH_3-9), 203.0 (C-1’), 32.1 (C-2’), 28.9 (C- 1’’), 121.9 (C-2’’), 131.7 (C-3’’), 17.8 (C-4’’), 25.8 (C-5’’), 71.8 (C-1’’’), 25.8 (C-2’’’), 25.7 (C-3’’’)[90]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
Patulinone F (**124**) $C_{18}H_{24}O_5$	*Melicope patulinervia* China[105]	^{1}H NMR (500 MHz, acetone-d_6) δ 3.24 (H-4) 3.12 (H-4), 4.73 (H-5), 2.64 (H-2’), 3.18 (H-1’’), 5.25 (H-2’’), 1.65 (H-4’’), 1.76 (H-5’’), 1.25 (H-2’’’), 1.26 (H-3’’’), 13.69 (OH-9) ^{13}C NMR (125 MHz, acetone-d_6) δ 106.0 (C-1), 155.4 (C-2), 104.4 (C-3), 28.0 (C-4), 91.5 (C-5), 165.9 (C-7), 103.6 (C-8), 165.1 (C-9), 203.5 (C-1’), 32.9 (C-2’), 22.5 (C-1’’), 123.6 (C-2’’), 131.2 (C-3’’), 25.9 (C-4’’), 17.9 (C-5’’), 71.6 (C-1’’’), 25.1 (C-2’’’), 26.4 (C-3’’’)[105]
Harronin I (**125**) $C_{23}H_{32}O_5$	*Harrisonia abyssinica* Kenya[106]	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (H-4 or H-3’), 3.03 (H-4 or H-3’), 4.68 (H-4 or H-3’), 1.51 (H-2’), 2.08 (H-3’), 5.09 (H-4’), 1.66 (H-6’), 1.24 (CH_3-1’), 3.22 (H-1’’), 5.20 (H-2’’), 1.76 (H-4’’), 1.72 (H-5’’), 2.60 (H-2’’’) ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.6 (C-1), 156.6 (C-2), 103.4 (C-3), 26.8 (C-4), 90.2 (C-5), 164.3 (C-7), 101.5 (C-8), 161.7 (C-9), 73.9 (C-1’), 37.1 (C-2’), 21.9 (C-3’), 123.1 (C-4’), 132.2 (C- 5’), 25.6 (C-6’), 17.6 (C-7’), 22.3 (CH_3-1’), 22.2 (C-1’’), 121.4 (C-2’’), 134.8 (C-3’’), 25.8 (C-4’’), 17.8 (C-5’’), 203.4 (C-1’’’), 32.8 (C-2’’’)[106]
Harronin II (**126**) $C_{23}H_{32}O_6$	*Harrisonia abyssinica* Kenya[106]	^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (H-4), 4.65 (H-5), 1.50 (H-2’), 2.08 (H-3’), 5.09 (H-4’), 1.66 (H-6’), 1.59 (H-7’), 1.25 (CH_3-1’), 3.20 (H-1’’), 5.18 (H-2’’), 1.76 (H-4’’), 1.69 (H-5’’) ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.0 (C-1), 159.2 (C-2), 104.1 (C-3), 26.7 (C-4), 90.3 (C-5), 165.5 (C-7), 103.0 (C-8), 162.0 (C-9), 73.9 (C-1’), 37.4 (C-2’), 22.0 (C-3’), 123.8 (C-4’), 132.9 (C-5’), 25.8 (C-6’), 17.6 (C-7’), 22.3 (CH_3-1’), 22.2 (C-1’’), 121.4 (C-2’’), 134.1 (C-3’’), 25.7 (C-4’’), 17.8 (C-5’’), 203.4 (C-1’’’), 68.2 (C- 2’’’)[106]
(*R*)-5-Deprenyllupulonol C (**127**) $C_{21}H_{30}O_5$	*Humulus lupulus* Germany[107] China[94]	^{1}H NMR (400 MHz, DMSO-d_6) δ 2.98 (H-6), 4.66 (H-7), 2.88 (H-2’), 2.79 (H-2’), 2.22 (H-3’), 0.91 (H-4’), 3.12 (H-1’’), 5.11 (H-2’’), 1.69 (H-4’’), 1.59 (H-5’’), 1.15 (H-2’’’), 1.18 (H-3’’’) ^{13}C NMR (100 MHz, DMSO-d_6) δ 100.5 (C-1), 161.2 (C-2), 104.0 (C-3), 158.2 (C-4), 106.9 (C-5), 27.1 (C-6), 90.7 (C-7), 160.7 (C-9), 203.5 (C-1’), 50.7 (C-2’), 25.1 (C-3’), 22.7 (C-4’), 22.5 (C-5’), 21.1 (C-1’’), 123.3 (C-2’’), 129.6 (C-3’’), 25.5 (C-4’’), 17.7 (C-5’’), 69.9 (C-1’’’), 24.8 (C-2’’’), 26.1 (C-3’’’)[94]
(*S*)-5-Deprenyllupulonol C (**128**) $C_{21}H_{30}O_5$	*Humulus lupulus* Germany[107] China[94]	
Patulinone G (**129**) $C_{18}H_{24}O_5$	*Melicope patulinervia* China[105]	^{1}H NMR (500 MHz, acetone-d_6) δ 3.17 (H-6), 3.10 (H-6), 4.81 (H-7), 2.59 (H-2’), 3.26 (H-1’’), 5.22 (H-2’’), 1.64 (H-4’’), 1.75 (H-5’’), 1.23 (H-2’’’), 1.36 (H-3’’’), 13.47 (OH-2) ^{13}C NMR (125 MHz, acetone-d_6) δ 102.4 (C-1), 162.8 (C-2), 108.2 (C-3), 158.8 (C-4), 104.9 (C-5), 27.8 (C-6), 92.3 (C-7), 162.4 (C-9), 202.7 (C-1’), 31.4 (C-2’), 22.2 (C-1’’), 124.3 (C-2’’), 131.1 (C-3’’), 26.0 (C-4’’), 18.0 (C-5’’), 71.5 (C-1’’’), 26.0 (C-2’’’), 26.3 (C-3’’’)[105]
(±)-Japonicol G (**130**) $C_{20}H_{28}O_5$	*Hypericum japonicum* China[96]	^{1}H NMR (400 MHz, CD_3OD) δ 3.02 (H-6), 4.70 (H-7), 3.98 (H-2’), 1.12 (H-3’), 1.14 (H-4’), 1.52 (H-2’’), 2.11 (H-3’’), 5.13 (H-4’’), 1.63 (H-6’’), 1.68 (H-7’’), 1.20 (H-8’’) ^{13}C NMR (100 MHz, CD_3OD) δ 105.5 (C-1), 156.3 (C-2), 161.4 (C-4), 105.6 (C-5), 27.7 (C-6), 91.9 (C-7), 168.2 (C-9), 212.1 (C-1’), 40.1 (C-2’), 19.9 (C-3’), 19.9 (C-4’), 74.4 (C-1’’), 39.5 (C-2’’), 23.1 (C-3’’), 125.7 (C-4’’), 132.6 (C-5’’), 17.8 (C-6’’), 26.0 (C-7’’), 22.0 (C-8’’)[96]
Acrophenone F (**131**) $C_{18}H_{20}O_5$	*Acronychia pedunculata* Taiwan[51]	^{1}H NMR[a] ($CDCl_3$) δ 7.61 (H-4), 2.65 (H-2’), 2.52 (H-4’), 3.47 (H-1’’), 5.25 (H-2’’), 1.78 (H-4’’), 1.62 (H-5’’), 4.18 (H-1’’’), 13.44 (OH-9) ^{13}C NMR[a] ($CDCl_3$) δ 110.2 (C-1), 156.9 (C-2), 109.3 (C-3), 112.2 (C-4), 151.9 (C-5), 159.4 (C-7), 107.3 (C-8), 161.7 (C-9), 205.0 (C-1’), 33.6 (C-2’), 188.3 (C-3’), 26.5 (C-4’), 22.1 (C-1’’), 121.2 (C-2’’), 132.5 (C-3’’), 17.9 (C-4’’), 25.8 (C-5’’), 60.5 (C-1’’’)[51]
Acronyculatin H (**132**) $C_{16}H_{18}O_4$	*Acronychia pedunculata* Thailand[83]	^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (H-4), 7.48 (H-5), 2.71 (H-2’), 3.52 (H-1’’), 5.32 (H-2’’), 1.68 (H-4’’), 1.82 (H-5’’), 4.16 (OCH_3-2), 13.30 (OH-9) ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.5 (C-1), 154.6 (C-2), 109.8 (C-3), 105,6 (C-4), 143.4 (C-5), 159.2 (C-7), 107.4 (C-8), 159.1 (C-9), 60.2 (OCH_3-2), 205.0 (C-1’), 33.3 (C-2’), 22.2 (C-1’’), 121.7 (C-2’’), 132.3 (C-3’’), 25.8 (C-4’’), 17.8 (C-5’’)[83]

Table 3. Prenylated-geranylated polycyclic phloroglucinol derivatives (cont.)

Phloroglucinol derivative Chemical formula	Species Geographic location	^{1}H and ^{13}C NMR data (chemical shift δ / ppm)
Faberione A (**133**) $C_{28}H_{32}O_4$	*Hypericum faberi* China[67]	^{1}H NMR[a] ($CDCl_3$) δ 7.01 (H-6), 4.06 (H-2’), 1.35 (H-3’ H-4’), 3.52 (H-1’’), 5.34 (H-2’’), 2.11 (H-4’’), 2.13 (H-5’’), 5.04 (H-6’’), 1.68 (H-8’’), 1.84 (H-9’’), 1.59 (H-10’’), 7.73 (H-2’’’ H-6’’’), 7.43 (H-3’’’ H-5’’’), 7.32 (H-4’’’), 14.26 (OH-2), 6.68 (OH-4) ^{13}C NMR[a] ($CDCl_3$) δ 101.1 (C-1), 163.2 (C-2), 108.3 (C-3), 155.3 (C-4), 111.8 (C-5), 98.6 (C-6), 153.4 (C-7), 153.5 (C-9), 22.0 (C-1’’), 121.5 (C-2’’), 140.5 (C-3’’), 39.7 (C-4’’), 26.2 (C-5’’), 123.6 (C-6’’), 132.5 (C-7’’), 25.8 (C-8’’), 16.3 (C-9’’), 17.8 (C-10’’), 130.2 (C-1’’’), 124.1 (C-2’’’ C-6’’’), 129.0 (C-3’’’ C-5’’’), 128.1 (C-4’’’), 207.6 (C-1’), 38.9 (C-2’), 19.0 (C-3’ C-4’)[67]
Faberione B (**134**) $C_{29}H_{34}O_4$	*Hypericum faberi* China[67]	^{1}H NMR[a] ($CDCl_3$) δ 7.01 (H-6), 3.95 (H-2’), 1.32 (H-3’), 1.97 (H-4’), 1.57 (H-4’), 1.00 (H-5’), 3.52 (H-1’’), 5.35 (H-2’’), 2.11 (H-4’’), 2.14 (H-5’’), 5.04 (H-6’’), 1.68 (H-8’’), 1.84 (H-9’’), 1.61 (H-10’’), 7.74 (H-2’’’ H-6’’’), 7.43 (H-3’’’ H-5’’’), 7.32 (H-4’’’), 14.37 (OH-2), 6.69 (OH-4) ^{13}C NMR[a] ($CDCl_3$) δ 101.6 (C-1), 163.2 (C-2), 108.3 (C-3), 155.3 (C-4), 111.8 (C-5), 98.6 (C-6), 153.5 (C-7), 153.5 (C-9), 207.5 (C-1’), 45.5 (C-2’), 16.6 (C-3’), 26.6 (C-4’), 12.0 (C-5’), 22.0 (C-1’’), 121.5 (C-2’’), 140.5 (C-3’’), 39.7 (C-4’’), 26.2 (C-5’’), 123.5 (C-6’’), 132.5 (C-7’’), 25.8 (C-8’’), 16.3 (C-9’’), 17.8 (C-10’’), 130.2 (C-1’’’), 124.1 (C-2’’’ C-6’’’), 129.0 (C-3’’’ C-5’’’), 128.1 (C-4’’’)[67]
Faberione C (**135**) $C_{28}H_{32}O_5$	*Hypericum faberi* China[67]	^{1}H NMR[a] ($CDCl_3$) δ 6.86 (H-6), 4.04 (H-2’), 1.34 (H-3’ H-4’), 3.51 (H-1’’), 5.34 (H-2’’), 2.10 (H-4’’), 2.12 (H-5’’), 5.04 (H-6’’), 1.68 (H-8’’), 1.84 (H-9’’), 1.59 (H-10’’), 7.61 (H-2’’’ H-6’’’), 6.90 (H-3’’’ H-5’’’), 14.19 (OH-2), 6.66 (OH-4) ^{13}C NMR[a] ($CDCl_3$) δ 101.3 (C-1), 162.9 (C-2), 108.4 (C-3), 155.3 (C-4), 112.1 (C-5), 97.0 (C-6), 153.8 (C-7), 153.4 (C-9), 207.8 (C-1’), 39.0 (C-2’), 19.2 (C-3’ C-4’), 22.2 (C-1’’), 121.8 (C-2’’), 140.6 (C-3’’), 39.9 (C-4’’), 26.4 (C-5’’), 123.8 (C-6’’), 132.6 (C-7’’), 25.9 (C-8’’) 16.5 (C-9’’), 17.9 (C-10’’), 123.5 (C-1’’’), 126.0 (C-2’’’ C-6’’’), 116.1 (C-3’’’ C-5’’’), 155.9 (C-4’’’)[67]
Faberione D (**136**) $C_{29}H_{34}O_5$	*Hypericum faberi* China[67]	^{1}H NMR[a] ($CDCl_3$) δ 6.85 (H-6), 3.93 (H-2’), 1.31 (H-3’), 1.96 (H-4’), 1.57 (H-4’), 0.99 (H-5’), 3.51 (H-1’’), 5.34 (H-2’’), 2.10 (H-4’’), 2.12 (H-5’’), 5.04 (H-6’’), 1.68 (H-8’’), 1.84 (H-9’’), 1.59 (H-10’’), 7.62 (H-2’’’ H-6’’’), 6.91 (H-3’’’ H-5’’’), 14.30 (OH-2), 6.85 (OH-4) ^{13}C NMR[a] ($CDCl_3$) δ 101.4 (C-1), 162.6 (C-2), 108.0 (C-3), 154.9 (C-4), 111.7 (C-5), 96.7 (C-6), 153.4 (C-7), 153.2 (C-9), 207.2 (C-1’), 45.3 (C-2’), 16.4 (C-3’), 26.4 (C-4’), 11.8 (C-5’), 21.8 (C-1”), 121.4 (C-2”), 140.2 (C-3”), 39.5 (C-4”), 26.0 (C-5”)123.4 (C-6”), 132.2 (C-7”), 25.5 (C-8”), 16.1 (C-9”), 17.6 (C-10”), 123.2 (C-1’’’), 125.7 (C-2’’’ C-6’’’), 115.7 (C-3’’’ C-5’’’), 155.5 (C-4’’’)[67]
Hyperannulatin C (**137**) $C_{25}H_{36}O_4$	*Hypericum annulatum* Rhodopi Mountain[35]	^{1}H NMR (600 MHz, $CDCl_3$) δ 5.96 (H-3), 2.72 (H-6), 2.38 (H-6), 1.77 (H-7), 1.51 (H-8), 1.35 (H-8), 1.46 (H-9), 1.28 (H-9), 1.79 (H-11), 1.47 (H-11), 4.15 (H-2’), 1.16 (H-3’), 1.14 (H-4’), 1.59 (H-1’’), 2.07 (H-2’’), 1.95 (H-2’’), 5.01 (H-3’’), 1.65 (H-5’’), 1.57 (H-6’’), 0.97 (H-1’’’), 1.02 (H-2’’’) ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.5 (C-1), 165.4 (C-2), 95.9 (C-3), 160.5 (C-4), 98.8 (C-5), 22.8 (C-6), 33.5 (C-7), 22.5 (C-8), 38.9 (C-9), 30.7 (C-10), 46.5 (C-11), 80.8 (C-12), 155.9 (C-14), 211.2 (C-1’), 38.3 (C-2’), 20.9 (C-3’), 18.8 (C-4’), 38.4 (C-1’’), 22.5 (C-2’’), 123.7 (C-3’’), 132.3 (C-4’’), 25.8 (C-5’’), 17.8 (C-6’’), 34.3 (C-1’’’), 27.7 (C-2’’’)[35]
Atrovirisidone (**138**) $C_{24}H_{26}O_7$	*Garcinia atroviridis* Malaysia[108]	^{1}H NMR (500 MHz, CD_3OD) δ 6.18 (H-3), 6.31 (H-5), 3.32 (H-1’), 5.00 (H-2’), 1.64 (H-4’), 1.71 (H-5’), 3.39 (H-1’’), 4.96 (H-2’’), 1.64 (H-4’’), 1.76 (H-5’’), 3.94 (C-1’’’) ^{13}C NMR (125 MHz, CD_3OD) δ 99.0 (C-1), 166.6 (C-2), 101.1 (C-3), 166.7 (C-4), 101.5 (C-5), 163.5 (C-6), 143.0 (C-8), 138.4 (C-9), 147.5 (C-10), 129.0 (C-11), 126.0 (C-12), 137.3 (C-13), 169.2 (C-15), 26.2 (C-1’), 124.0 (C-2’), 132.2 (C-3’), 25.8 (C-4’), 18.0 (C-5’), 26.5 (C-1’’), 123.6 (C-2’’), 132.9 (C-3’’), 25.9 (C-4’’), 18.3 (C-5’’), 62.9 (C-1’’’)[108]
Atrovirisidone B (**139**) $C_{24}H_{26}O_7$	*Garcinia atroviridis* Malaysian[109]	^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (H-3), 6.34 (H-5), 3.48 (H-1’), 5.22 (H-2’), 1.71 (H-4’), 1.83 (H-5’), 3.53 (H-1’’), 5.22 (H-2’’), 1.74 (H-4’’), 1.87 (H-5’’), 3.78 (H-1’’’), 11.01 (OH-2), 5.65 (OH-10) ^{13}C NMR (125 MHz, $CDCl_3$) δ 99.7 (C-1), 165.9 (C-2), 100.6 (C-3), 163.1 (C-4), 101.0 (C-5), 162.3 (C-6), 145.1 (C-8), 118.6 (C-9), 145.4 (C-10), 142.5 (C-11), 125.4 (C-12), 136.3 (C-13), 168.4 (C-15), 24.1 (C-1’), 121.7 (C-2’), 133.1 (C-3’), 26.0 (C-4’), 25.9 (C-5’), 23.4 (C-1’’), 121.9 (C-2’’), 133.2 (C-3’’), 26.0 (C-4’’), 18.3 (C-5’’), 62.0 (C-1’’’)[109]

[a]Magnetic field strength was not found in the reference. NMR: nuclear magnetic resonance.

values between 23 and 36 µM.[101] Exploration of the aerial parts of *H. pseudopetiolatum* (CH_3OH) resulted in the antimicrobial **112**, and from *H. yojiroanum* (CH_3OH), compound **113**.[102,103] Metabolites **133-135** were isolated from CH_3OH extracts of *H. faberi* along with **118** and **136** and demonstrated moderate cytotoxic (PANC-1).[67]

Derivatives **92** and **127-128** have been associated with ethanolic extracts of *Humulus lupulus* (female inflorescences), the only species of the genus related to polycyclic phloroglucinols.[94] *Harrisonia abyssinica* is another unique species of its genus correlated with this class of metabolites; however, two studies were performed, with hexanoic root extract (resulting in **93**) and with CH_3OH/CH_2Cl_2 1:1 fruit extract (resulting in **125-126**); the last two compounds have antimicrobial action against *C. albicans* (MIC of 5 µg mL^{-1} for **125** and > 100 µg mL^{-1} for **126**) and *B. cereus* (MIC of 6 µg mL^{-1} for **125** and > 100 µg mL^{-1} to **126**).[95,106] As previously described species, *Bosistoa selwyn* is the only one of the genera in this research and provided compound **107** from petroleum ether extracts (leaves).[99] From the genus *Garcinia*, **138-139** were isolated in methanolic extracts from the roots of *G. atroviridis*; furthermore, **138** exhibited cytotoxicity against HeLa cells and mildly inhibitory to *B. cereus* and *S. aureus*, and **139** showed cytotoxic activity against human breast (MCF-7), human prostate (DU-145) and human lung (H-460).[108,109]

Regarding the genus *Acronychia*, only two species were studied: CH_3OH/CH_2Cl_2 (1:1) extracts of *A. trifoliolata* bark resulted in **121**, cytotoxic molecules **105-106** (moderate antiproliferative cytotoxic activity against NCI-60), and also compound **108**.[53,100] Extraction of leaves and branches of *A. pedunculata* using CH_3OH resulted in compounds **119** and **132**; when extraction was performed using roots and acetone, compounds **120**, **122-123** and **131** were isolated.[51,83] Considering the genus *Melicope*, three specimens were isolated: **114** from methanolic extracts of leaves and branches of *M. ptelefolia*, **117** from leaves of *M. barbigera* in CH_2Cl_2, and **124** and **129** from CH_3CH_2OH extracts of the leaves of *M. patulinervia*.[92,104,105]

5. Spectroscopic Discussion

The compiled and standardized ^{13}C NMR data of acylphloroglucinol derivatives are of great value for structural elucidation purposes. These spectroscopic patterns will facilitate the structural characterization of future isolated compounds and their identification in extracts or impure fractions. This is due to the presence of signals in the NMR spectra associated with similar structural fragments in multiple compounds of this class, such as the THB core and the acyl chain. On the other hand, the basic units of polycyclic acylphloroglucinols resemble benzofurans, benzopyrans and benzopyranones, but are hydroxylated. For spectroscopic data analysis, the aromatic carbon attached to the acyl group was defined as C-1 for all acylphloroglucinols compiled in this review.

5.1. Prenylated and geranylated monocyclic acylphloroglucinol derivatives

Monocyclic derivatives of acylfloroglucinol **1-88** are formed by common fragments, for example, the THB core. As a result, similar chemical environments are perceived in carbons with corresponding positions of different structures. The analysis of the ^{13}C NMR (150 MHz, $CDCl_3$) data for compounds **3**, **18**, **20**, **29**, **48**, **50**, **57**, **60-61**, **63-64**, and **74** confirms this fact. Considering the reduced THB unit, three unprotected oxygenated carbons are observed in the aromatic ring (104.0-109.8 ppm in C-1, 95.1-106.9 ppm in C-3, and 95.1-106.3 ppm in C-5) and three non-oxygenated carbons, commonly protected by the electron density donor effect of neighboring *ortho*-hydroxyls (157.6-164.5 ppm in C-2, 160.1-164.5 ppm in C-4 and 159.0-164.9 ppm in C-6).

Common substituents also showed spectroscopic similarities in different structures. The acyl group can be recognized by the most unprotected sign of the carbonyl at 200.7-210.8 ppm ($CDCl_3$ and 150 MHz), although values are seen in lower field than those observed for compounds **28**, **63-64** and **78-81**. The prenyl group commonly replaces the hydrogens attached to the aromatic carbons or oxygens of THB. Considering the conditions of 100 MHz and $CDCl_3$ for compounds **65-70** and **75-76**, due to the better relationship between data resolution and the number of compounds for evaluation, intervals of chemical shifts for the carbons are observed: when connected directly to the THB, signals are recorded in 121.67-123.4 ppm (mono-hydrogenated olefinic), 131.3-135.6 ppm (non-hydrogenated), 21.6-23.1 ppm (methylene), and 17.9-25.9 ppm (two methyl groups); on the other hand, compared to the previous situation, oxygen-bounded prenyl in **75-76** show significant higher chemical shift at 65.3-65.4 ppm (C-1), while other signals are seen at 118.6-118.7 ppm (C-2), 138.5-138.7 ppm (C-3), 18.1-18.2 ppm (C-4), and 25.7 ppm (C-5), which are consequence of the lower influence of oxygen atom.

Substitutions of the hydrogens at aromatic carbons in 1,3,5-trihydroxybenzene by geranyl result in patterns like those observed for the prenyl group. Because of this, the comparative relationship of the C-1 of geranyl linked to carbon and oxygen, such as for **64** and **80**, respectively, is similar to the situations previously reported, including the values of chemical shifts. Although the geranyl derivatives present two isomeric forms, the *E* stereoisomers are more commonly found than the *Z* isomers, verified only in compounds **21** and **24**, due to a probable energetic favoring. Furthermore, considering the analysis at $CDCl_3$ and 150 MHz, ten carbon signals referring to this substituent were observed in metabolites **18**, **20**, **60-61**, **63-64** and **74**: 21.5-22.4 ppm (C-1), 121.4-121.9 ppm (C-2), 139.2-140.1 ppm (C-3), 39.6-39.7 ppm (C-4), 26.2-26.3 ppm (C-5), 123.5-123.6 ppm (C-6), 131.9-132.1 ppm (C-7), 25.6 ppm (C-8), 16.1-16.2 ppm (C-9) and 17.6-17.7 ppm (C-10).

5.2. Bicyclic and tricyclic acylphloroglucinol derivatives

Polycyclic compounds **89-139** have different structures, making it difficult to standardize their numbering. This diversity is due to multiple cyclization mechanisms, in which the acyl group may contributes directly (**89-93**, and **138-139**) or indirectly (**94-137**) for the formation of the polycyclic ring.[114] Despite this, the spectroscopic signals of the prenyl and geranyl substituents are characteristic and perceived when evaluating the NMR data. In addition, only **105** and **106** showed alkoxy groups, represented by a characteristic hydrogen singlet signal, with chemical shift values at 3.75-3.72 ppm for H-2 and H-10, respectively.

6. Conclusions

Acylphloroglucinol derivatives were compiled in this review along with their biosynthetic, taxonomic, bioactivity, structural, chemical and spectroscopic information. In nature, can generated from malonyl CoA decarboxylative condensation, and structural changes in the THB core and side chains proceed by different types of natural reactions, such as: alkylation, acylation, alkoxylation, prenylation, geranylation and cyclization. Taxonomically, they are associated with different genera and species of plants, in addition to presenting significant biological activities. Structurally, common fragments such as the THB core and substituents such as prenyl and geranyl are observed, which suggests interesting patterns for spectroscopic analysis. This information highlights the relevance of the topic of this review, which can be explored as a guide for studies involving this class of metabolites.

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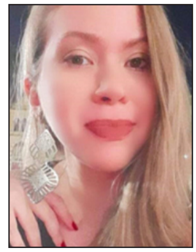

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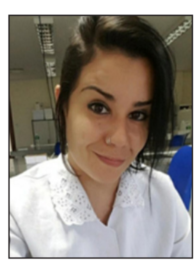

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